

CATALYTIC SURFACE COATINGS FOR HOUSEHOLD OVENS

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ABSTRACT

CATALYTIC SURFACE COATINGS HOUSEHOLD OVENS

The emission of harmful volatile compounds, such as aldehydes, and also carbon monoxide could occur during cooking processes at home or industry due to the combustion and cracking of spilled vegetable oil on the walls of an oven. It is known that the by-products generated during cooking could affect human health and environment if they are properly vented or removed. To eliminate the health and environmental problems related to oven emission, self-cleaning catalytic materials coated walls for ovens seem to be viable alternative to the toxic and time consuming chemical cleaning solutions.

In this project, a sol-gel method and also the dip coating technique was used to produce a catalytic material coated aluminum plates. Specifically, the calcination time and the temperature were studied to better understand the relationship between the textural/chemical properties of the catalyst coated metal plates and their catalytic activities. The studied calcination temperatures were 450°C, 500°C and 550°C whereas the calcination time were 10 min, 30 min and 60 min for each type of catalyst. Aluminum oxide supported nickel and also aluminum oxide - manganese oxide supported nickel catalysts were prepared as the catalyst that were used in coating. The catalytic activities of the catalyst coated plates were determined using canola oil as a function of reaction time which were 1h at 170°C and 200°C. The results have been shown that the most convenient calcination conditions for the canola oil combustion were 500°C for 30 minutes by using aluminum oxide – manganese oxide supported nickel catalyst.

ÖZET

EV TİPİ FIRINLAR İÇİN KATALİTİK YÜZEY KAPLAMALARI

Evlerde veya endüstride yemek yapılma sürecinde aldehit, karbon monoksit gibi birçok zararlı kimyasal uçucu bileşik ortaya çıkmaktadır. Bu uçucu kimyasallar yemek pişirilmesi esnasında fırınların yüzeylerine yapışıp birikmektedirler. Bu durum hem kimyasal açıdan insan sağlığını tehdit ederken, diğer bir yandan temizlik ürünleri kullanımını arttırmakta, mali ve iş gücü bakımından israfa yol açmaktadır. Aynı zamanda açığa çıkan kimyasal uçucu bileşikler doğaya da zarar vermekte, atmosferde sera etkisi yaratmaktadır. Bu sebeplerden dolayı, yemek pişirilmesi esnasında ortaya çıkan zararlı gazların veya partiküllerin ortadan kaldırılması gerekmektedir. Bu bağlamda kendi kendini temizleyen fırın teknolojisi, insan ve çevre sağlığı, aynı zamanda ekonomik getirisi açısından önemli bir rol oynamaktadır.

Bu çalışmada, ev tipi fırınlar için kendi kendine temizlemeyi sağlayan kaplama malzemeleri üretimi çalışılmıştır. Bu kaplamalar sayesinde, yemek pişirilmesi esnasında ortaya çıkıp, fırın duvarlarına yapışan, yağ damlalarının ve yağ buharının, uçucu ve zararlı hidrokarbonlara dönüşmeden kontrollü miktarlarda karbon dioksit çevrilerek, ortamdan uzaklaştırılması hedeflenmiştir. Kaplama malzemeleri katalitik malzemeler olup sol-jel tekniğiyle hazırlanmıştır. Çalışılan kaplama malzemeleri alüminyum oksit destekli nikel katalizörü ve alüminyum oksit – manganez oksit destekli nikel katalizörüdür. Fırın yüzeyini simüle etmek amacıyla katalizörler alüminyum plakalara sabit daldırma ve çıkarma hızıyla kaplanmıştır. Kalsinasyon sıcaklığı ve süresi çalışılarak kaplana katalizörlerin kimyasal ve yüzeysel özelliklerinin daha iyi anlaşılması hedeflenmiştir. Çalışılan kalsinasyon sıcaklıkları 450°C, 500°C and 550°C ve süreleri ise 10 dk, 30 dk ve 1 saattir. Kanola yağının plakalar üzerindeki yanma reaksiyonu gözlemlenmiş ve maksimum dönüşüm alüminyum oksit – manganez oksit destekli nikel katalizörü ile 84% olarak gözlemlenirken, alüminyum oksit destekli nikel katalizör maksimum 73% yağ dönüşümü sağlamıştır.

TABLE OF CONTENTS

LIST OF FIGURES.....	viii
LIST OF TABLES.....	x
CHAPTER 1. INTRODUCTION.....	1
CHAPTER 2. LITERATURE SURVEY.....	7
2.1. Volatile Organic Compounds (VOCs).....	7
2.2. Catalytic Combustion of VOCs.....	8
2.3. Catalysts of VOCs Combustion.....	10
2.3.1. Noble Metal Catalysts.....	10
2.3.2. Metal Oxide Supported Catalysts.....	12
CHAPTER 3. MATERIALS AND METHODS.....	18
3.1. Materials.....	18
3.2. Methods.....	19
3.2.1. Preparation of Aluminum Metal Surface for Sol-Gel Coatings.....	19
3.2.2. Preparation of Catalysts.....	19
3.2.2.1. Preparation of Pure Alumina.....	18
3.2.2.2. Preparation of Alumina Supported Nickel Catalyst and Aluminum Manganese Oxide Supported Nickel Catalyst.....	20
3.2.3. Preparation of Catalysts Coated Plates.....	20
3.2.4. Coating of Plates.....	21
3.2.5. Oil Combustion on Catalyst Coated Plate.....	23
3.2.6. Characterization of the Catalysts.....	23
3.2.6.1. Gas Chromatography – Mass Spectroscopy (GC-MS)	23
3.2.6.2. Scanning Electron Microscopy (SEM).....	24
CHAPTER 4. RESULTS AND DISCUSSION.....	25

4.1. Pure Alumina Catalyst.....	27
4.2. Aluminum Oxide Supported Nickel Catalyst.....	31
4.3. Aluminum Oxide -Manganese Oxide Supported Nickel Catalyst.....	35
4.4. Reusability of the Catalyst.....	43
4.5. Factorial Analysis of the Study.....	44
CHAPTER 5. CONCLUSION.....	49
REFERENCES.....	51

LIST OF FIGURES

<u>Figure</u>	<u>Page</u>
Figure 1.1. Scheme of VOC removal techniques (Khan et al. 2000).....	3
Figure 3.1. Image of dip-coating process with Nima Dip-coater equipment.....	21
Figure 3.2. Catalyst coated samples preparation scheme.....	22
Figure 3.3. Images of catalyst coated aluminum plates.....	23
Figure 4.1. Images of droplet size difference impact on the surface after reaction.....	26
Figure 4.2. (a) Conversion vs. Time graph for small amount droplet size of oil @170°C, (b) Conversion vs. Time graph for large amount droplet size of oil @170°C.....	26
Figure 4.3. Calcination time versus conversion plot for pure alumina samples calcined at 450°C, 500°C and 550°C.....	28
Figure 4.4. Calcination temperature versus conversion plot for pure alumina samples calcined for 10min, 30min, and 60min.....	29
Figure 4.5. XRD Patterns for pure alumina coated samples calcined at 450°C, 500°C, and 550°C for 30 min.....	30
Figure 4.6. SEM images of (a) fresh Pure Alumina coated plate and (b) regenerated Pure Alumina coated plate.....	30
Figure 4.7. EDX Analysis of (a) fresh pure alumina coated plate and (b) regenerated Pure Alumina coated plate.....	31
Figure 4.8. Calcination time versus conversion plot for 20% Ni/Al ₂ O ₃ samples calcined at 450°C, 500°C and 550°C.....	32
Figure 4.9. Calcination temperature versus conversion plot for 20% Ni/Al ₂ O ₃ samples calcined for 10 min, 30 min, and 60 min.....	33
Figure 4.10. XRD Patterns for 20%Ni/Al ₂ O ₃ coated samples calcined at 450°C, 500°C, and 550°C for 30 min.....	34
Figure 4.11. SEM images of (a) fresh 20% Ni/Al ₂ O ₃ coated plate and (b) regenerated 20%Ni/Al ₂ O ₃ coated plate.....	34
Figure 4.12. EDX Analysis of (a) fresh 20% Ni/Al ₂ O ₃ coated plate and (b) regenerated 20% Ni/Al ₂ O ₃ coated plate.....	35

Figure 4.13. Calcination time vs conversion plot of 20%Ni/56% Mn_xO_y /Al ₂ O ₃ Samples calcined at 450°C, 500°C and 550°C.....	36
Figure 4.14. Calcination temperature vs conversion plot of 20%Ni/56% Mn_xO_y /Al ₂ O ₃ samples calcined for 10, 30, 60 min.....	37
Figure 4.15. GC-MS chromatogram of combustion of oil at 170°C for 1h by using 20%Ni/56% Mn_xO_y /Al ₂ O ₃	38
Figure 4.16. GC-MS chromatogram of combustion of oil at 200°C for 1h by using 20%Ni/56% Mn_xO_y /Al ₂ O ₃	38
Figure 4.17. GC-TCD chromatogram of combustion of oil at 200°C for 1h by using 20%Ni/56% Mn_xO_y /Al ₂ O ₃	39
Figure 4.18. XRD Patterns for 20%Ni/56% Mn_xO_y /Al ₂ O ₃ coated samples calcined at 450°C, 500°C, and 550°C for 30 min.....	40
Figure 4. 19. XRD Patterns of fresh pure alumina, 20%Ni/Al ₂ O ₃ , and 20%Ni/56% Mn_xO_y /Al ₂ O ₃ coated samples.....	41
Figure 4. 20. XRD Patterns for regenerated pure alumina, 20%Ni/Al ₂ O ₃ , and 20%Ni/56% Mn_xO_y /Al ₂ O ₃ coated samples.....	41
Figure 4.21. SEM images of (a) fresh 20%Ni/56% Mn_xO_y /Al ₂ O ₃ coated plate and (b) regenerated 20%Ni/56% Mn_xO_y /Al ₂ O ₃ coated plate.....	42
Figure 4.22. EDX Analysis of (a) fresh 20%Ni/56% Mn_xO_y /Al ₂ O ₃ coated plate and (b) regenerated 20%Ni/56% Mn_xO_y /Al ₂ O ₃ coated plate.....	42
Figure 4.23. Reusability Plot of Catalysts Prepared by 30 min of Calcination @170°C for.....	43
Figure 4.24. Interaction plots for conversion of oil combustion reaction.....	46
Figure 4.25. Main effects plot for conversion of oil combustion reaction.....	46
Figure 4.26. Residual plots for conversion of oil combustion reaction.....	48

LIST OF TABLES

<u>Table</u>	<u>Page</u>
Table 2.1. Catalysts for VOCs Combustion.....	10
Table 3.1. Chemicals and their properties used in catalyst synthesis and combustion reaction.....	17
Table 4.1. Operating conditions of canola oil combustion reaction.....	25
Table 4.2. Conversion data of small droplets and large droplets at 170°C for 1h.....	26
Table 4.3. Canola oil conversion data over alumina coated plates.....	28
Table 4.4. Canola oil combustion data for 20% Ni/Al ₂ O ₃	32
Table 4.5. Canola oil combustion data for 20%Ni/56%Mn _x O _y /Al ₂ O ₃	36
Table 4.6. Factors and Levels.....	44
Table 4.7. Analysis of Variance for all interactions and factors.....	45
Table 4.8. Analysis of Variance for selected interactions of factors.....	45
Table 4.9. Model Summary of selected interactions of factors.....	47

CHAPTER 1

INTRODUCTION

In recent years the improvement in technology has advantages for humanity to provide comfort in daily life and ease of processes. However, it may have critical effects for humanity and nature. Enlarging of the population increases the consumption of natural sources which leads to altering of ecological balance. The improvements and the consumptions cause many of undesired outlets such as byproducts. Those byproducts can have dangerous impacts on human health and environment in short term or long term. The most common examples for those dangerous byproducts are outdoor exhaust gases which are greenhouse gases and toxic gases such as high concentrated CO₂ and NO_x. Many of the processes present in the industry or the daily life of humanity cause the releasing of greenhouse and toxic gases to the atmosphere. So that, the environmental issues such as air pollution become a global concern. Especially, the emissions of the outlets derived from the chemical reactions causing the air pollution with harmful effect on the environment and the human health.

Volatile organic compounds (VOCs) are get involved in the class of air pollutants. VOCs are the chemical compounds including carbon, hydrogen and oxygen. VOCs have different classes of compounds with different properties and chemistry, however they influence the atmosphere with the same effect. Since those compounds have long term and short term impacts on human health and environment, regulations are allowed by the governments to prevent greenhouse effect. United States regulates by Environmental Protection Agency (EPA). EPA has been working for the protection of the environment due to increasing concerns because of globalization and civilization. United States Environmental Protection Agency (US EPA) indicates that a VOC based on their relative photochemical reactivity in the atmosphere. In European region the regulations are altered. European Union (EU) explains VOCs according to volatility and reactivity which is any organic compound that possess a vapor pressure of 0.01 kPa or more at 293.15 K. In Turkey, Kyoto Protocol is applied in order to regulate the VOC emission levels.

Since VOCs are relatively higher photochemical reactivity, their emissions cause photochemical smog which is induced by the stratospheric ozone depletion and formation of ground level ozone. Therefore, the VOCs emissions lead to an increment on global greenhouse effect. The VOCs are permanent and stable in the environment. The effects of VOCs on human health are classified as long term and short term. The toxic nature of the VOCs are causing headache, dizziness, nausea, eye and skin irritations, respiratory system damages, lung and heart diseases, neurological effects and cancer that are resulted in long or short term. Furthermore, the VOCs are not only affecting the outdoor living, but also influence the indoor activities. Many researches have been demonstrated that people working inside the buildings have diseases and allergies due to VOCs and other air pollutants such as asbestos, CO, formaldehyde, NO_x, SO₂, radon which is called Sick Building Syndrome (SBS).

The content of VOCs have large variety of different organic and inorganic molecules. The existing VOCs in the atmosphere are mainly caused by industrial processes, organic solvent usages and combustion sources which include hydrocarbon based fossil fuels. The VOC emissions can be both caused by the biogenic and anthropogenic sources. Biogenic sources include plants, trees, wild animals, natural forest fires and anaerobic processes. Those incidents are hard to control. On the other hand, the emissions caused by anthropogenic sources such as human activities such as transport, evaporation, solvent usage, industrial processes that are oil refining or chemical manufacture, petrol storage and distribution, landfilled wastes, food manufacture and agriculture can be control by the conscious of humanity.

In daily life, vegetable oils are used for cooking and baking purposes. The cooking processes that especially involve oil consumption are leading to VOC removals. As it is well known cooking is a heat involved process in which oil is heated for a large time period by exposing them to the surrounding air. According to the chemical and physical properties of the removals that are released to the atmosphere, they are transporting by rain, snow or as a gas or particulate matters. The VOCs and NO_x may cause acid rain and photochemical smog by the reaction of them in the presence of sunlight to form ozone and peroxy compounds. Therefore, the environment and humanity are affected by them directly or indirectly.

The fried and baked food outlets generate considerable amount of VOC during the cooking process. In daily life, cooking processes emit oil and grease mists from fats.

This emissions from cooking processes leads to many of unsaturated hydrocarbons removal that is a form of VOCs. This removals are very reactive in photochemical processes and causes photochemical smog (Kolar, 2008).

In order to eliminate the VOCs several treatment methods exist. In fact, the generated VOC concentration differs from plant to plant due to their different capacity and operating conditions. So that, according to process of interest, VOCs emissions are tried to be prevented or minimized to volatilization, at this point, equipment adjustments or emission control techniques are applied. In Figure 1.1, the scheme for removal techniques for VOC are shown. The main idea of the VOC destruction techniques generally converting VOCs into carbon dioxide and water whereas, recovery techniques is aimed to provide reusing and subsequent disposal of VOCs. The most commonly used type of VOC removal techniques in industry are adsorption, bio-filtration, thermal reduction and catalytic combustion. The other techniques are limited due to their harsh and relatively expensive operating conditions (Khan et al. 2000).

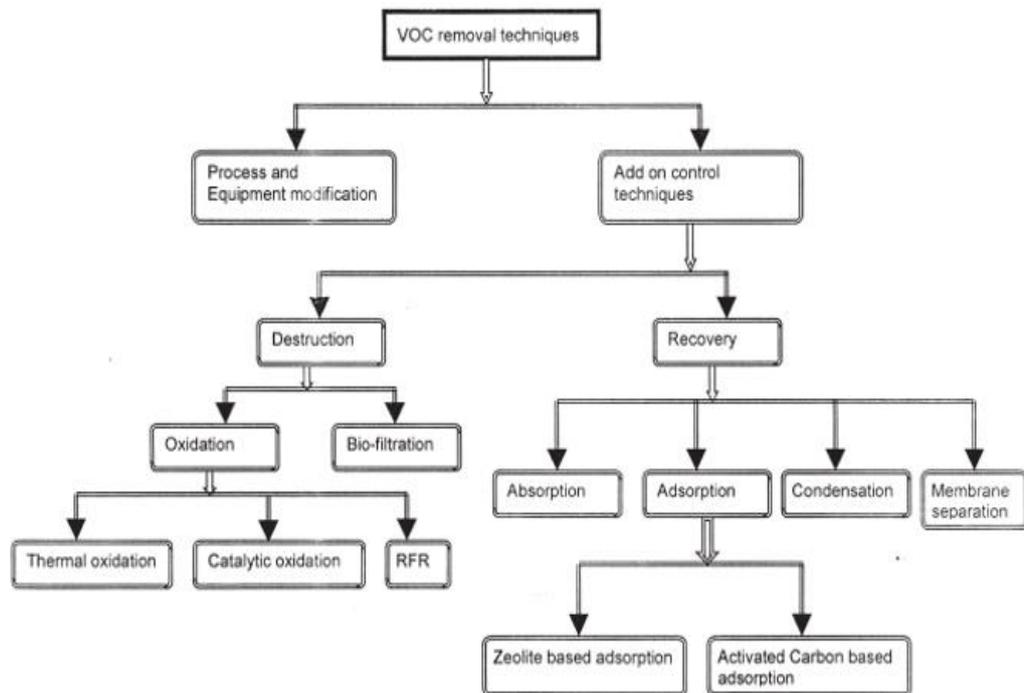


Figure 1.1. Scheme of VOC removal techniques
(Source: Khan et al. 2000)

Among those techniques used for VOC elimination, catalytic oxidation is one of the promising methods. Since catalytic VOC oxidation has several advantages such as lowering the oxidation temperature in contrast to thermal oxidation, so that cost reduction

and energy saving is obtained with this method (Khan et al. 2000). In addition to this, its results are efficient and effective by consuming lower energy for the VOC removal. The NO_x emission reduction is achieved by catalytic oxidation (Sharma et al. 1995). There are some parameters must be taken into account during the VOC catalytic oxidation reaction such as the concentration of VOC, space velocity, temperature, type of catalyst, extent of reducibility of the catalysts, and the catalyst loading.

In order to eliminate the VOCs by the catalytic oxidation reaction, the structure of VOC of interest should be considered since reactivity of VOCs changes with their functional groups. The reactivity of VOCs can be aligned from highest to lowest as alcohols, aromatics, ketones, carboxylic acids, alkanes, respectively. The conversion VOCs into desired product is affected by concentration of VOCs, space velocity and the temperature. During the combustion, C-H bonds of saturated hydrocarbons are broken, so that the strength of C-H bonds is significantly important. Strong C-H bonds require high catalytic activity for the oxidation reaction with high temperature (Khan et al. 2000). However, the most crucial parameter is the catalyst type used since the reaction is occurred on the surface of the catalyst. The crucial part of this technique is to selection of convenient catalyst. Since the oxidation is occurred on the surface of the catalyst, the catalysts are chosen according to nature of pollutants and reaction conditions. For this sense, the catalysts used for VOC oxidation can be classified as; noble metals, metal oxides, supported metals and also mixtures of noble metals and metal oxides. It is known that noble metal catalysts such as platinum, palladium are much active than the metal oxides. However, their poisonous nature leads to environmental aspects. Also, noble metals are more expensive than the metal oxides (Ibrahim et al., 2011). So that, nowadays, researches have been focused on the metal oxide catalysts for the oxidation such as manganese, nickel, copper, cerium, iron and etc. the selection of the catalysts are full filled by considering the activity of catalyst. According to the studies, the catalytic activity depends on active phase, loading, specific surface area of catalyst, the dispersion of active compound and promoters (Larsson et al. 2000). The many of the researches were accomplished by investigating effects of those parameters on catalytic oxidation of VOCs. Nowadays, nickel and manganese oxide catalyst are attentional types of metal oxide catalysts with suitable supports such as aluminum oxide.

Nowadays, development of domestic electrical appliances market is improving day by day. Since the globalization and the competition among the producers to maintain

the position in the market become very important concern. So that this competition brings brand new concerns about the production of innovative products and value added accessories in addition to primary functions of the products. Those value added properties generally covers the benefits of the customer and usability of the product. The cooking appliances is one the important issue in electrical appliances market since, the food consumption is an essential process for the daily life of the humanity. In this case, the cleaning of household cooking appliances is one of the most attentional issue for both manufacturers and the customers. During the cooking process many of the carbonaceous species accumulate over the oven surfaces. The fats or other species present in the food are released during the cooking. The VOCs are also example for this releasing compounds. The VOCs are thermally degraded due to cooking temperatures up to 300°C which causes difficulties for the cleaning purposes. This cooking outlets causes not only dirt and odor accumulation but also, they effect the human health negatively. The accumulated dirt inside oven are cleaning by traditional cleaning materials such as caustic detergents. Today in electronic appliance market, self-cleaning ovens are began to implementing as pyrolytic cleaning system where accumulated organics are removed by high temperature implementation for 1 to 3 hours by turning the species into dust (Palmissano et al., 2011). In spite this technology is promising, it has disadvantages in terms of safety, cost and high levels of energy consumption issues.

Many of researchers have been stated that sol-gel method is convenient for alumina preparation in terms of catalyst carrier synthesis in contrast to traditional preparation methods. Since generally controlled pore size distribution and surface area are necessary for the catalytic reactions involved alumina, sol-gel method is appropriate for this requirement. Sol-gel process is a widely used technique in the material science, also called as chemical deposition which is involved in the fabrication of materials that generally metal oxides starts from a chemical solution acting as precursor for integrated network of discrete particles or network polymers. The sol-gel process involves two states which are sol and gel. Sol is a colloidal suspension of solid particles in a liquid where dispersion of solid particles in a liquid that only Brownian motion suspend the particles whereas gel state involves both liquid and solid particles dispersed in each other including three-dimensional solid network that contains liquid components.

In this thesis study, instead of producing VOCs from oil combustion, a new technology has been developed which prevents VOCs formation over metal oxide

catalysts for household ovens. In other words, self-cleaning technology was developed for household ovens. For this purpose catalytic coating materials were prepared by sol-gel method. Pure alumina, aluminum supported nickel catalyst, and aluminum – manganese oxide supported nickel catalysts were prepared in sol state and coated over aluminum plates and their conversions were investigated for oil combustion reaction. The effect of calcination temperature, calcination duration and the reaction temperature were investigated on catalytic conversion on the coated plates.

CHAPTER 2

LITERATURE SURVEY

2.1. Volatile Organic Compounds (VOCs)

Volatile organic compounds (VOCs) are the chemicals with the content of hydrogen, carbon and other elements. Volatile organic compounds are easily evaporative and their boiling points are in the range of 50-100°C to 240-260°C. Also, the saturation vapor pressures of VOCs are larger than 102kPa at 25°C. Fossil fuel deposits, plants, vegetation, volcanoes, bacteria and etc. can be the natural sources of VOCs, on the other hand, transportation emissions, solvent usage, evaporation of gasoline and many of the industrial processes such as oil based paints or solvents are the synthetic sources of the VOCs. Acetone, benzene, ethylene glycol, formaldehyde, methylene chloride, toluene, xylene and 1,3-butadiene are the most common types of VOCs.

VOCs have dangerous impact on human health and environment. Since, VOCs including many of compounds with different chemistry and property, they affect the atmosphere as greenhouse gases. VOCs have long-term and short-terms health effects on humanity such as eye, nose, throat, skin irritations, headaches, nausea, damaging of liver, kidney and central nervous system, furthermore, cause cancer due to their chemical content.

Since, the negative impact of VOCs on environment and human health, some regulations are allowed by the governments for the protection of human health and environment. In U.S., Environmental Protection Agency (EPA) and in Europe, United Nations Economic Commission for Europe (UNECE) have protocols for those regulations. In Turkey, Kyoto Protocol is applied for VOCs regulations.

Most of the VOCs have no distinguishable odor whereas some of the odors of VOCs have very at low levels. The VOCs are photo-chemically sensitive compounds, so that their reaction with nitrogen oxides and sunlight can be provide the formation of ozone and other products.

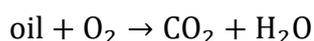
In order to allow low concentration levels of VOCs in indoor and outdoor some of preventions must be taken. Choosing low emission materials for furnishing, cleaning and the construction, provide the reducing of indoor levels of VOC concentrations.

There are several techniques to eliminate the VOC emissions which involves recovery or destruction of them. There are traditional and technological studies for VOC elimination techniques. For instance, packed tower aeration or mechanical surface aeration allow VOC emissions treatment by using contaminated liquid are some examples of VOC treatments. On the other hand, VOC contaminant liquids can be exposed to activated carbon adsorption or air stripping and if VOC is soil contaminant then soil vapor extraction (SVE) is used. From another point of view, to provide degradation of VOCs into compounds that are less dangerous such as carbon dioxide, water and hydrochloric gases, VOCs are treated with thermal or internal oxidation, catalytic or UV oxidation (Berenjian et al. 2012). The most reliable technique for VOC elimination is the catalytic oxidation.

2.2. Catalytic Combustion of VOCs

The treatment of VOCs are very difficult since VOCs and hydrocarbon based deposit have very complex index. Although the combustion process of VOCs have very expensive equipment and high operation and maintenance costs, it is a one of the most promising treatment to eliminate the VOCs.

In daily life, baking and cooking processes involve oil combustion. In this case, oil deposits are taken into account as VOCs. The oil have very complex structure as chemical that includes many of saturated and unsaturated fats. Also they have sensitivity to oxygen and light. In the combustion reaction of oils, oxygen is involved reacting with oil to generate the compounds such as carbon dioxide and water. The possible reaction would be as following (Yang et al. 2004):



To accomplish this reaction a suitable catalyst is needed. Since the catalytic oxidation reaction occurs on the surface of the catalyst among adsorbed VOCs and oxidant. As thermodynamically known as catalysts reduce the activation energy barrier

to allow the reaction by involving different paths. Allowing a suitable catalyst diminishes the temperature requirement of oxidation reaction.

The most critical parameter involved in catalytic combustion process is the catalyst for the treatment of the related disposal. Therefore, for the improvement of the process, the catalyst selection is a crucial step. For the oxidation reaction a convenient catalyst must be chosen. This catalyst needs to be active and selective for this reaction. So that, the nature of catalyst has an importance. Also the catalyst involved in the reaction is required to be convenient for operation conditions. For combustion reaction, oil needs to be thermally stable (Morales et al, 2006).

The catalytic reactions are required several steps. Firstly, the diffusion of the reactants from bulk fluid to the catalyst surface or the catalyst pores. Then subsequently, the reaction was accomplished on catalyst surface to form products and then, the products are diffused from the catalyst surface by desorption.

As mentioned before, the VOCs are reacting with the oxidant over the surface the catalyst of interest in catalytic oxidation. According to the individual properties of the catalysts, the reaction rate is determined. In literature, the oxidants used in catalytic combustion are ozone, oxygen, hydrogen peroxide and UV.

There are many studies on catalytic combustion for VOCs. The studies are mainly focused on noble metal and metal oxide catalysts. According to studies, the noble metals have high performance on catalytic combustion process in terms of high activity, selectivity and conversion. However, noble metal catalysts are expensive. Also, noble metals have low stability and poisonous catalysts. So that, the researchers have been focused on transition metal and metal oxide catalysts to improve their activity, stability and conversion. Also, transition metals and metal oxides have lower costs compared to noble metals.

Currently, manganese, nickel, copper, cobalt, chromium, acidic oxides like zeolites and $\text{TiO}_2/\text{SiO}_2$ are the most commonly studied oxides with their mixed oxides. However, they have some critical points such as low activity, non-reusability, and deactivation during the process and etc. in VOC combustion. Furthermore, new metals are involved in the oxidation processes such as tungsten which has ability to preventing catalyst poisoning in the presence of sulfur dioxide (Everaert et al. 2004).

2.3. Catalysts of VOCs Combustion

The catalysts involved in the oxidation reactions can be classified by two categories as mentioned before which are indicated in Table 2.1.

Table 2.1. Catalysts for VOCs Combustion

Noble Metal Catalysts	Metal Oxides - Transition Metal Oxides
Pt, Pd, Rh, Au	Mn, Cu, Ni, Fe, Ce, Al, Zn, Co, La, Sr, W

2.3.1. Noble Metal Catalysts

Noble metal catalysts are commonly used type of catalysts which have high activity and selectivity for catalytic combustion reaction. Zhang et al. (2007) have been studied to noble metals which were Au, Rh, Pd, Pt/TiO₂. They have prepared the catalysts with the impregnation method. The catalyst were involved in catalytic combustion of formaldehyde. The catalytic performances of the catalysts were investigated in terms of catalytic activities. The catalytic activity of the catalysts were determined according to adsorption of the species on the catalyst surface during the reaction carried out at the room temperature. Their study have been revealed that the catalytic activity of the species were in the following order with 1 wt. % Pt/TiO₂>Rh/ TiO₂>PdTiO₂>AuTiO₂> TiO₂.

As seen also seen in study of Zhang et al. (2007), platinum is known as one of the most promising catalyst for the catalytic studies. The performance of the platinum was proved by also Papaefthimiou et al. (1998). They were investigated Pt supported on γ -Al₂O₃, SiO₂, TiO₂ and TiO₂ (W⁶⁺) catalysts for the benzene and ethyl acetate combustion. The catalytic activity of Pt catalysts was researched for the benzene and ethyl acetate oxidation. The catalytic activity of Pt have been improved by the doping of TiO₂ support with W⁶⁺ cations. The highest value of the activity was reached when the content of catalyst was 0.45% in TiO₂ support. In this study, during the reaction of combustion of ethyl acetate the TiO₂ with W⁶⁺ cation provides a variety in product distribution. Adding W⁶⁺ cations causes decomposition of ethyl acetate to intermediate products such as ethanol, ethylene, and acetaldehyde, because W⁶⁺ cations provides an increment of active sites on the catalyst support surface. On the other hand, during the ethyl acetate oxidation,

the highest oxygen chemisorption is observed over TiO_2 with W^{+6} cation. The activities of the catalysts are investigated by Turn over Frequency (TOF). TiO_2 with W^{+6} cations show stable properties. According to results, doping of catalysts was not influenced the reaction path. This was proved by the doped and undoped catalysts providing the similar kinetic properties during the oxidation of VOCs. The activity of Pt catalyst doped with W^{+6} is more active since for the reactions of ethylacetate, acidic sites are necessary and doping with WO_3 provides more active sites. In another study, Pt and Pd loaded catalysts were also investigated by Sharma et al. (1995). Their catalysts were bimetallic hydrophobic catalysts that single Pt, Pd catalysts and Pt-Pd bimetallic catalysts for the combustion of VOCs which were methanol, acetone and methylene chloride. They are involved in the reaction as single component VOC or two or three component mixtures with atmospheric pressure and temperature range of 50-400°C which provides 90% conversion of methanol and acetone and 60% methyl chloride at 400°C. Due to alloy effect of Pt-Pd bimetallic catalyst, the highest activity was provided by this one. They have been claimed that presence of hydrocarbon in the system promote the oxidation of metallic Pt catalysts which less active oxide included surface complex. VOC oxidation is highly exothermic reaction therefore the impact of external heat transfer limitations are remarkable especially, at lower feed rates, so that for the elimination of this case, different runs were carried out with the temperature range of 50-400°C. The reaction kinetics were investigated by using semi-empirical Langmuir-Hinshelwood model. The inhibition and promotion impacts on three VOC mixture were considered to obtain rate equation. They have premised that reduction properties are related with concentration of active sites which means higher reduction property provides higher promoting impact on conversion and increasing reduction capability rises the concentration of effective metallic Pt on surface.

Although noble metal catalysts are effective for VOC combustion purposes however due to economic aspects development of metal oxide catalysts is the trending objective (Ferrandon 2001).

2.3.2. Metal Oxide Supported Catalysts

Nowadays, mixed transition – metal oxides are widely used for catalytic combustion instead of noble metals due to their cheaper, environmentally friendly and active nature. Metal oxides are convenient for combustion applications, fine chemical synthesis, controlling the emissions and chemical waste (İbrahim et al., 2011).

Alumina is a commonly used catalyst and catalyst support material in catalyst chemistry for industry. Since alumina has features such as surface area, pore volume, pore size distribution, textural properties, acid-base characteristics, it provides convenient surface chemistry and phase composition for study of interest. Also alumina has chemical and thermal stability for reactions. The main phases of the alumina widely used in catalytic activities are α -Al₂O₃, η -Al₂O₃ and γ -Al₂O₃. Among those three phases the most stable one is the α -Al₂O₃ with its crystalline structure. α -Al₂O₃ is commonly used in the applications which requires low surface area and high temperature such as steam reforming. The other phases of the alumina are transitional which have spinel-like structure with altering order that layers are stacked. (Chorkendorff, et al.,2003)

The studies have been shown that the transition metal-oxides to be highly active in catalysis of oxidation of hydrocarbons and VOCs. Furthermore, 3d-transition metal oxides which compose of cations in their higher oxidation state were accomplished the highest catalytic performance. (Mehandijiev, 1997)

For the combustion of hydrocarbons and VOCs, manganese oxides such as Mn₃O₄, Mn₂O₃ and MnO₂ are commonly preferred due to their high activity. The researches were revealed that the combustion reaction of VOCs and hydrocarbons over manganese oxide produce CO₂ with total oxidation reactions. Manganese oxides have capability to generate oxide with altering oxidation states and oxygen storage capacity. Thus, manganese oxides are used in a wide range of applications such as catalyst, structural and electronic promoters in heterogeneous catalytic reactions. Manganese oxides are preferable in catalytic activities since they have high efficiency in the reduction/oxidation cycles. Since their redox capabilities can be promoted by applying them with the combinations of other elements such as Ni, Fe, Co and etc. In addition to this, the applications such as ozone decomposition, CO and organic pollutant oxidation,

reduction of nitric oxide which are carried out by manganese based catalysts have not negative impact on environment and human health (Morales et al., 2007).

On the other hand, nickel is widely preferred in catalytic applications due to its nature. Since nickel provides synthetic transformations such as cross coupling reactions including carbon-carbon bonds and it reduces the electron rich carbon bonds. The most active metal oxide has been determined as NiO for the total oxidation of VOCs due to its high reactivity with the deficiency of electrons in the lattice (Solsana, 2011). Mehandjiev (1997) has been stated that nickel oxidation states are Ni(0), Ni(II), Ni(III), and Ni(IV). For the catalytic applications nickel oxides coupled with manganese oxides were commonly studied and they have two types of crystal structures. The first crystal structure is spinel; NiMn_2O_4 where the ions are distributed among tetrahedral and octahedral spinel sites and the second one is ilmenite; NiMnO_3 where the ions are located in octahedral positions (Mehandjiev, 1997).

Morales et al. (2006) studied catalytic combustion of ethanol and propane in presence of Manganese-Copper mixed oxides. The catalysts were prepared by co-precipitation method by changing aging time. They have preferred co-precipitation method since it provides high inter-dispersion of copper and manganese elements which provides various arrangements between the phases. Their results have shown that the catalytic activity is improved by increasing aging time. They compared the catalytic performance of Mn-Cu mixed oxides with pure Mn_2O_3 and pure CuO oxides in order to effect of aging time. They concluded that mixed oxides had shown higher performance than the pure samples. This is due to the nature of formed structure which causes high dispersion on catalytic surface by time, so that the catalytic activity improved by aging. Again co-precipitation method was used by Morales et al. (2007) for the synthesis of manganese iron or nickel mixed oxide catalysts by altering the aging time. They investigated catalytic combustion of propane and ethanol as volatile organic compound. According to their results, for the propane combustion MnNi catalyst was shown better performance while for ethanol combustion MnFe was shown better performance in terms of catalytic activity. However, in this study, the aging time was not significantly affected to the catalytic activity. Investigation of the nickel manganese mixed oxide crystal structure and catalytic performance for the oxidation reaction of ethyl acetate, benzene and carbon monoxide were accomplished by Mehandjiev et al. (1998).

The catalysts were prepared with ilmenite (NiMnO_3) and spinel ($\text{Ni}_x\text{Mn}_{3-x}\text{O}_4$) structure which were highly dispersive to analyze the crystal structure by using carbonate precursors with co-precipitation method. Their study has been claimed that ilmenite oxides with high dispersion were more active for catalytic combustion and it has better crystallinity. The crystallinity of ilmenite has been poor around 400°C , however, by increasing the temperature to $500\text{--}600^\circ\text{C}$ causes decomposition into spinel oxide despite the crystallinity increases for Mn:Ni is 1. For spinel structure catalyst, appropriate crystallinity is provided around at 750°C . The higher activity of ilmenite type catalysts was reached due to stabilized manganese ions in a higher oxidation degree. Thus the manganese ions pretend as active sites during the combustion reaction.

In another study, combustion of CO, ethyl acetate and ethanol were carried out over $\text{CuO}_x/\text{Al}_2\text{O}_3$, $\text{CuO}_x\text{--CeO}_2/\text{Al}_2\text{O}_3$, $\text{CuMn}_2\text{O}_4/\text{Al}_2\text{O}_3$ and $\text{Mn}_2\text{O}_3/\text{Al}_2\text{O}_3$ catalysts (Larsson et al., 2000). Larsson et al. claimed that catalytic activity enhancing by loading CuO_x where crystalline CuO particles were obtained. Their results were indicated that for CO combustion $\text{CuO}_x\text{--CeO}_2/\text{Al}_2\text{O}_3$ catalyst has higher activity than the $\text{CuMn}_2\text{O}_4/\text{Al}_2\text{O}_3$ whereas $\text{CuMn}_2\text{O}_4/\text{Al}_2\text{O}_3$ has more activity than $\text{CuO}_x\text{--CeO}_2/\text{Al}_2\text{O}_3$ for ethyl acetate and ethanol combustion. $\text{CuO}_x/\text{Al}_2\text{O}_3$ and $\text{CuO}_x\text{--CeO}_x/\text{Al}_2\text{O}_3$ catalysts were prepared by dry impregnation method and $\text{CuMn}_2\text{O}_x/\text{Al}_2\text{O}_3$ catalyst was prepared with co-impregnation method. $\text{CuO}_x/\text{Al}_2\text{O}_3$ catalyst was loaded with copper of 3, 6 and 18 mmol Cu/m^2 which is indicated as Cu3Al, Cu6Al and Cu18Al. The activity of catalyst which is prepared by addition of alumina to ceria before deposition of copper oxide is improved the complete CO combustion due to well distribution of copper oxide species. In this case, for ethyl acetate and ethanol combustion, the ceria is not much affected. The active sites of the catalysts are differed, therefore electronic and synergetic effects have an impact on combustion of the compounds. In another study, VOCs such as propyl alcohol, toluene and cyclohexane catalytic oxidation was performed via nanoparticles of $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ ($x = 0, 0.2$) which are prepared by co-precipitation method with absence of support (Huang et al. 2007). The highest activity was shown by $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_3$ in catalytic combustion with following sequence: propyl alcohol > toluene > cyclohexane. This order was obtained due to bond strengths of C-C and C-H bonds. Their examination also was also shown that the activity of $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_3$ is provided by preparation via partial substitution of Sr for La at the active sites of LaCoO_3 that provides large vacancies of oxygen. According to results, it was indicated that the energy required to break the

weakest C-H bond is regulates the rate of combustion of VOCs where the highest energy required to break the weakest C-H bond belongs to cyclohexane.

Kim et al. (2001) also have been studied on different metal catalyst production for catalytic oxidation of aromatic hydrocarbons. They have been investigated the catalytic activity of Cu, Mn, Fe, V, Mo, Co, Ni, Zn / Al₂O₃ metal catalysts on benzene, toluene and xylene complete combustion. Catalytic activities of catalysts are researched according to varying calcination temperature. Since rising the calcination temperature, lower the specific surface areas of catalysts. However, increasing calcination temperature lowers the reaction conversion. So that they have considered disappearing of active sites when calcination temperature increases and specific surface area decreases. Also catalytic activities are induced by differing copper loadings on Al₂O₃. The most active catalyst has been found as 5wt% of Cu/Al₂O₃ due to well dispersion of copper surface because of smaller particle size of copper. In combustion of VOC molecules, the activity of %wt. Cu/Al₂O₃ is indicated by toluene>xylene>benzene.

Buciuman et al. (1999) have been studied on hopcalite-type that is mixed copper and manganese oxide catalyst for CO and H₂ oxidation reactions. The catalysts are highly active and they have redox mechanism. Lattice oxygen is involved during the reaction over Mn₂O₃ that is related with adsorbed oxygen species. They proposed a model that explained as manganese oxide is oxygen donator and copper oxide is oxygen acceptor to explain the highly activity of hopcalite catalysts.

Nourreddini et al. (1999) have been studied for liquid phase catalytic oxidation in contrast to most of the studies. They are synthesized various transition metal and metal oxide catalysts which are tungsten, tantalum, and their oxides, molybdenum, zirconium, niobium where alumina pellets and kieselguhr powder are used as support. The catalysts were involved for the combustion of oleic acid with hydrogen peroxide to produce azelaic and pelargonic acids. Among the prepared catalysts the highest activity and selectivity is provided by tungsten and tungstic oxide. Tungstic oxide supported silica for the oxidation of oleic acid has 85% conversion with high selectivity to azelaic acid. The reaction rate of alumina supported catalyst is lower since average pore diameter of alumina is lower than the silica which caused lower reaction rate. Furthermore, due to settling down of alumina pellets the contact area is decreased and slow down the reaction. The activity behaviors of supported and unsupported catalysts are not similar since pore diffusion resistance due to support initially.

Yang et al. (2004) have been studied for the treatment of cooking oil fume by low temperature catalysts. The catalytic oxidation was investigated over MnO_2/CuO catalyst by varying oil temperatures, catalyst temperature and time on the cooking oil fume. According to their results, removal of high temperature oil is difficult. They have concluded that the catalyst is mineralized into several organics if the contact time is appropriate within the convenient temperature range of the reaction.

For the cleaning purposes of household ovens self-cleaning properties are provided by catalytic combustion of oil from food outlets. For this, Palmisano et al. (2009) have been developed MnCr_2O_4 , LaFeO_3 and CeO_2 catalysts which are prepared by solution combustion synthesis method in order to oxidase the myristic (tetracanoic), palmitic (hexadecanoic) and stearic (octadecanoic) acids. Performances of the catalysts were investigated by catalytic activity over fatty acid combustion and with different reaction conditions. The activities of the prepared samples were measured by TPC method with 1:9 w/w of fatty acid and powder catalyst to obtain similar properties with real oven surfaces and to improve reproducibility. The coating was carried out with spray pyrolysis which is appropriate for the production of inorganic compounds over surfaces. In order to prevent excess precursor solution and droplet formation, the spraying time was determined by observation. Also to improve adhesion properties of the surface for the catalytic combustion reaction and to provide complete crystalline structure of catalysts, the coated samples exposure to 600°C of heat treatment. In this study it was observed that mass transport has minor effect due to geometrical conditions which catalyst and reactants in the solid state. According to analysis, CeO_2 has higher crystallinity than LaFeO_3 and MnCr_2O_4 as high as complexity of crystal structure. Therefore, CeO_2 provides the best adhesion properties and the highest activity over fatty acid combustion. They have been also investigated pork lard and olive oil combustion processes where MnCr_2O_4 has provided highest conversion. Again Palmisano et al. (2011) have been developed CeO_2 powder catalyst which is synthesized by solution combustion synthesis to obtain high specific surface areas with presence of any carrier in order to improve thermal oxidation of solid food soil. CeO_2 has profits in terms of economic aspects. Also the studies were shown that CeO_2 catalyst enhances the oxidation efficiency for all types of food outlets. The best adhesion properties and the highest dispersion properties are gained by urea decomposition method out of sol-gel, powder coating, and gel combustion methods. The reaction was carried out in multiple stages, in first stage, the reaction kinetics are higher

due to direct oxidation of organic compounds. Next steps were relatively slower due to harder oxidation properties of intermediates which are oxides in higher temperatures. Therefore the temperature of second stage was not the same for every case. They been also experienced the different type of food outlets such as vegetable outlets like tomato and oil based food outlets, consequently the experiments were carried out with oil based foods have been indicated lower performance. They have been concluded that by using CeO_2 catalyst with 400°C and 1 hour of operation time provide self-cleaning properties for all food outlets.

CHAPTER 3

MATERIALS AND METHODS

3.1. Materials

Preparation of Ni/Al₂O₃ and Ni-Mn_xO_y/Al₂O₃ by modified single step sol-gel method was involved in this study. Also pure Al₂O₃ was synthesized as reference catalyst to compare with the other samples. In the sol-gel method, precursor was aluminum isopropoxide (Alfa Aesar) for alumina, solvent was deionized water (DIW) and peptizer was nitric acid (HNO₃) for the all the catalysts. In preparation of Ni/Al₂O₃ catalysts nickel (II) acetate monohydrate (Alfa Aesar) was involved as precursor for nickel and in preparation of Ni-Mn_xO_y/Al₂O₃, manganese (II) nitrate tetrahydrate (Merck) was involved as precursor for manganese oxide. For the oil combustion, commercial canola oil was used. In Table 3.1 the chemicals and their properties used for the catalyst synthesis and combustion reaction were shown.

Table 3.1. Chemicals and their properties used in catalyst synthesis and combustion reaction

Chemicals	Chemical Formula	Molecular Weight (g/mol)	Purity (%)
Aluminum Isopropoxide	Al(OCH(CH ₃) ₂) ₃	204.24	98
Nitric Acid	HNO ₃	63.01	65
Nickel (II) Acetate Monohydrate	Ni(CH ₃ COO) ₂ .1H ₂ O	194.69	99
Manganese (II) Nitrate Tetrahydrate	Mn(NO ₃) ₂ .4H ₂ O	251.01	96

3.2. Methods

The experimental work of this study covers following steps:

- Preparation of aluminum plate surfaces for coating
- Preparation of catalysts in sol state as coating material
- Coating of the aluminum plate surfaces with the sol stated catalysts
- Oil combustion reaction over catalyst coated aluminum plates.

3.2.1. Preparation of Aluminum Metal Surface for Sol-Gel Coating

Aluminum metal plates were placed into aqueous commercial detergent at 66°C for 30 minutes in ultrasonic bath. Aluminum plates were immersed in deionized water at 38°C for 5 minutes and then sprayed with deionized water at ambient temperature. The plates were etched with alkaline etchant solution at 66°C for 20 minutes in ultrasonic bath and again plates were rinsed by immersing in deionized water at ambient temperature for 5 minutes. The alkaline etchant processes were accomplished by preparing a mixture of 45g/l of NaOH and 2.45 g/l of EDTA and dipping the plates for 7 minutes at 66°C in ultrasonic bath, then 0.05 of NaNO₃ was added to the solution at 66°C and plates were kept for 23 minutes. After etching the Aluminum plates were de-smutted with 35% of HNO₃ acid at 66°C for 4 minutes in ultrasonic bath and plates were rinsed by immersing in deionized water at ambient temperature for 5 minutes. Finally the plates were kept in deionized water at 95°C for 2 hours.

3.2.2. Preparation of Catalysts

3.2.2.1. Preparation of Pure Alumina

Pure alumina coated plates was prepared as blank sample for the comparison of the other catalysts. All the catalyst were prepared by the same sol-gel method which were coated on the plates in the sol state.

To prepare the pure alumina sol first of all, 80 ml of H₂O was heated to 85°C on heating plate in a shot bottle and then 8.176 g of aluminum iso-propoxide (AIP) was added to water and stirred with 1500 rpm for an hour. 0.5130 ml of nitric acid (HNO₃) added to the mixture at 85°C and stirred at 1500 rpm for an hour. Then, 14.54 g of 1,3-butandiol was added to the solution at 85°C and stirred at 1500 rpm for an hour.

3.2.2.2. Preparation of Alumina Supported Nickel Catalyst and Aluminum – Manganese Oxide Supported Nickel Catalyst

The same procedure was applied to prepare the alumina supported nickel catalyst and the alumina and manganese supported nickel catalyst by sol-gel method. 80 ml of water was heated to 85°C and 8.176 g of AIP was added to the solution and stirred at 1500 rpm for an hour. Then 0.5130 ml of nitric acid was added to the mixture and stirred at 1500rpm and 85°C for an hour. 14.54 g of 1, 3-butandiol was added to the mixture at 85°C under 1500 rpm and kept for an hour. To prepare the alumina supported nickel catalyst, after 15 minutes 0.837 g of nickel was added to the mixture to obtain 20 wt. % nickel in the final alumina supported nickel catalyst at 85°C at 1500 rpm. Similarly, to prepare the aluminum – manganese oxide supported nickel catalyst, firstly 0.25 g of nickel was added to mixture and stirred at 85°C and 1500 rpm for 15 minutes and then again after 15 minutes, 3.33 g of manganese precursor was added to the mixture at 85°C and 1500 rpm which was corresponding to 20 wt. % nickel and 56 wt. % manganese oxide in the final alumina-manganese oxide supported nickel catalyst.

3.2.3. Preparation of Catalysts Coated Plates

Aluminum plates were coated with prepared sols by dip-coating method. The coating process was accomplished by Nima Dip Coater with fixed immersing and withdrawal speed which were set according to the viscosity of the prepared sol to obtain uniform coating thickness. The coating processes by Nima Dip Coater can be seen in Figure 3.1.



Figure 3.1. Image of dip-coating process with Nima Dip-coater equipment

Aluminum plates were dipped with 150 mm/min of speed into certain sol which was desired to be coated and kept in the sol for 120 second, to finalize the coating the metal plates were raised with 150 mm/min of withdrawal speed. The coated plates were dried at 120°C for 30 minutes. After drying process the plates were calcined with the calcination temperatures of 450°C, 500°C, and 550°C for 10 minutes, 30 minutes and 60 minutes. For each types of sol, the same coating procedure was applied with the same parameters.

3.2.4. Coating of Plates

The dip-coating procedure was applied by using Nima Dip-Coater equipment. The speeds of dipping and withdrawal were set according to viscosities of sol of interest. The controlling interface was supplied by LabView® software. The aluminum plates was dipped with 150 mm/min of speed and kept in the sol for 120 seconds. Then the plates were raised with again constant speed of 150 mm/min. The coatings were accomplished at room temperature. The speed of dipping and withdrawal were determine the thickness of the coatings on the plates. All of the plates were coated by pure alumina firstly, and

then alumina supported nickel catalyst and aluminum – manganese oxide supported nickel catalysts.

The coated plates were dried at 120°C for 30 minutes. After drying, the plates were calcined according to experiment parameters. The calcination was carried out at for 10 minutes, 30 minutes and 60 minutes for each type of coated catalyst to determine the effect of calcination temperature. Also the calcination temperatures for each sample was applied at 450°C, 500°C and 550°C. In Figure 3.2., the scheme of preparation of catalyst coated samples were shown.

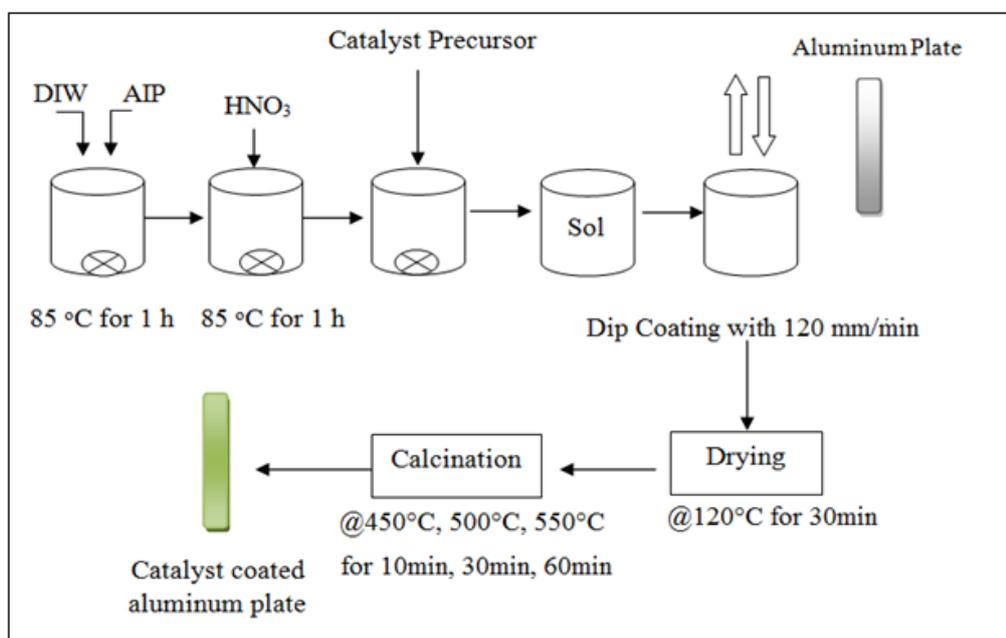


Figure 3.2. Catalyst coated samples preparation scheme

In Figure 3.3., the images of pure alumina coated, aluminum oxide supported nickel catalyst coated and manganese oxide – aluminum oxide supported nickel catalyst coated aluminum plates were indicated.



Figure 3.3. Images of catalyst coated aluminum plates

3.2.5. Oil Combustion on Catalyst Coated Plate

In order to test the performance of the sol coated plates, canola oil combustion was accomplished. A specific combustion set-up was adjusted to collect the outlet gases of the combustion over coated plates. The oil droplets were kept in 0.5 – 4.0 mg. The reaction temperatures were 170°C and 200°C to consider the effect of reaction temperature on catalyst conversion by taking account the real working conditions of the household ovens. The reaction was carried out over coated plates with dropping given amounts of canola oil by excess air in the adjusted set-up with given reaction temperatures. The plates were weighted before and after the combustion to determine conversion of the oil over the coated plates to obtain the performance of the catalysts. The regeneration process was carried out according to the calcination temperature of each individual set-up after combustion.

3.2.6. Characterization of the Catalysts

3.2.6.1. Gas Chromatography – Mass Spectroscopy (GC-MS)

Gas Chromatography – Mass Spectroscopy (GC – MS) is a technique which involves a gas chromatograph (GC) coupled with mass spectrometer (MS) to separate,

identify and quantify the complex mixtures of the chemicals. Especially, for the relatively lower molecular weighted compounds present in environmental materials are analyzed by this method. GC – MS provides the analysis of sufficiently volatile and thermally stable compounds.

3.2.6.2. Scanning Electron Microscopy (SEM)

Scanning Electron Microscope (SEM) investigates on beam of high energy electron to generate a variety of signals at the surface of solid specimens. In order to provide information about the sample including external morphology, chemical composition and crystalline structure and orientation of materials composing the sample, SEM is used by signals deriving from electron sample interactions. The collected data over a selected area of surface of sample and 2-dimensional image is obtained which displays spatial variations in the related properties. The surface areas are ranging from approximately 1 mm to 5 microns in the width is imaged in scanning mode using conventional SEM techniques. The SEM analysis were performed in order to investigate the surfaces of the coated plates with catalyst of interests.

CHAPTER 4

RESULTS AND DISCUSSION

The oxidation of canola oil over metal oxide and mixed metal oxide supported metal catalysts was studied. The catalysts were prepared by sol-gel method which provides to control of chemical reactions and textural and chemical properties of the catalyst. For each of the catalyst alumina used as support material since it has high stability. In the commercial applications alumina is the most commonly used support material. Also alumina support has very useful mechanical properties and highly disperse the active metal and metal oxide phases.

The oil combustion reaction was carried out at 170°C and 200°C by considering the average meal cooking temperature in household ovens. Aluminum plates were coated to simulate the oven walls during the cooking procedure. The batch system was implemented for the oil combustion reaction with constant temperature. Required amount of oil droplets were dropped to the aluminum plates which were about 10mg to 35mg. In Table 4.1., the operating conditions of the canola oil combustion reaction were given.

Table 4.1. Operating conditions of canola oil combustion reaction

Operating Parameters	Operating Value
Reaction temperature	170 - 200°C
Reaction time	1h
Amount of oil	10 - 35 mg

The main idea of the process was combustion of the attached oils over the oven walls by converting into CO₂ in the presence of metal oxide catalysts which provides self-cleaning ability in practice. Therefore, the catalyst selection was a crucial factor for the oil combustion reaction. The performance of studied catalysts which were pure alumina, aluminum oxide supported nickel and aluminum oxide – manganese oxide supported nickel catalysts were evaluated by their catalytic conversion in the canola oil combustion reaction. Hence, the most suitable catalyst was selected by its catalytic conversion.

To evaluate the worst scenario in the ovens, large amount of oil droplets were added to the coated aluminum plates. Since during the cooking process only oil mists attach to the oven walls which can be easily removed from surface compared to the large oil droplets. In Table 4.2., the conversion data was given for large droplets and small droplets at 170°C for 1h of reaction.

Table 4.2. Conversion data of small droplets and large droplets at 170°C for 1h

	Large Droplet		Small Droplet	
	Conversion (%)		Conversion (%)	
	1h	2h	1h	2h
Al_2O_3	49	52	33	57
20% Ni/ Al_2O_3	62	66,4	50	83
20%Ni/56%Mn ₂ O ₃ / Al_2O_3	63	71,5	67	100

In Figure 4.1, the image of the difference between large and small droplets added plates after the combustion reaction was shown.

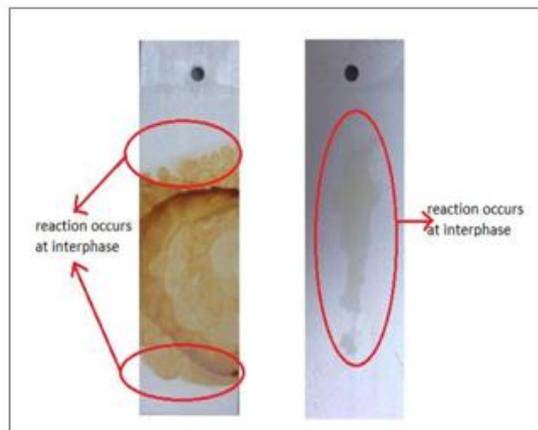


Figure 4.1. Images of droplet size difference impact on the surface after reaction

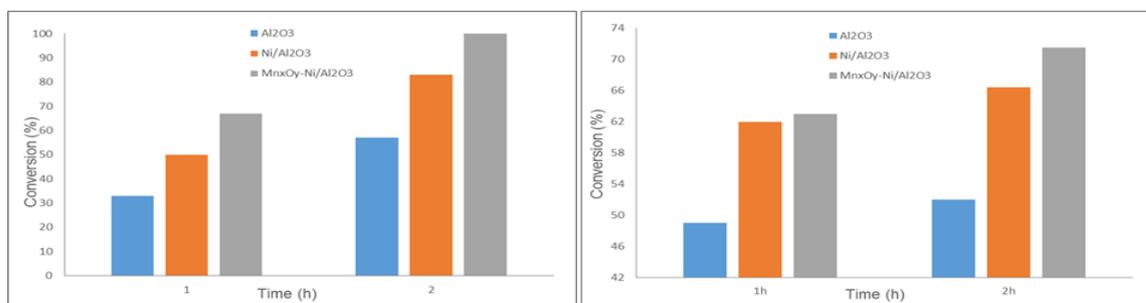


Figure 4.2. (a) Conversion vs. Time graph for small amount droplet size of oil @170°C
(b) Conversion vs. Time graph for large amount droplet size of oil @170°C

The conversion behavior of large droplets and small droplets were given in Figure 4.2. Large amount of droplet size causes the spreading of oil all of the coated active metal surface area which overflows from edges of coated metal plates. Therefore, the surface area for reaction occurring on the catalyst surface become lower. On the other hand, small amount of droplet size spreads on the active surface of coated plate and it was not overflow from the surface edges and it leads to higher active surface area to react. High surface area is an important factor for catalytic reaction since the reaction occurs at the interface.

During the catalyst preparation in order to active the catalyst coated plates, calcination step is involved. The calcination provides linking and network formation among the molecules. Since the C-C bonds of the oil during the combustion requires to be broken, the molecular positions has a crucial importance. The interactions between the molecules and their positions were highly affected by the calcination step. Therefore the catalytic activity of the coating materials are induced by the calcination step involved in their preparation.

The impact of calcination time and calcination temperature on catalyst performance in terms of catalytic conversion were investigated. This provides to define the optimum preparation conditions for the catalyst of interest which was used in the oil combustion reaction. The studied calcination temperatures for each type of catalyst were 450°C, 500°C and 550°C whereas the studied calcination times were 10min, 30min, and 60min.

4.1. Pure Alumina Catalyst

In order to provide controlled experimental set-up, pure alumina coated samples were used. Since, it is expected that alumina is not active for the oil combustion reaction for the conversion into CO₂ due to its nature. Therefore, alumina coated plates were employed in the experiments as blank samples with absence of catalyst precursor. In Table 4.3., the conversion data for the canola oil combustion was indicated whose reaction was carried out on the pure alumina coated plate at 200°C for 1h.

Table 4.3. Canola oil conversion data over alumina coated plates

Al ₂ O ₃ @450°C		Al ₂ O ₃ @500°C		Al ₂ O ₃ @550°C	
Time (min)	Conversion (%)	Time (min)	Conversion (%)	Time (min)	Conversion (%)
10	21	10	11	10	17
30	50	30	35	30	53
60	50	60	31	60	44

In Figure 4.3., the oil conversion behavior of pure alumina calcined at 450°C, 500°C and 550°C with different calcination times of 10min, 30min and 60min was shown. As it can be seen in the Figure 4.3., pure alumina coated plates provide maximum oil conversion as 53%.

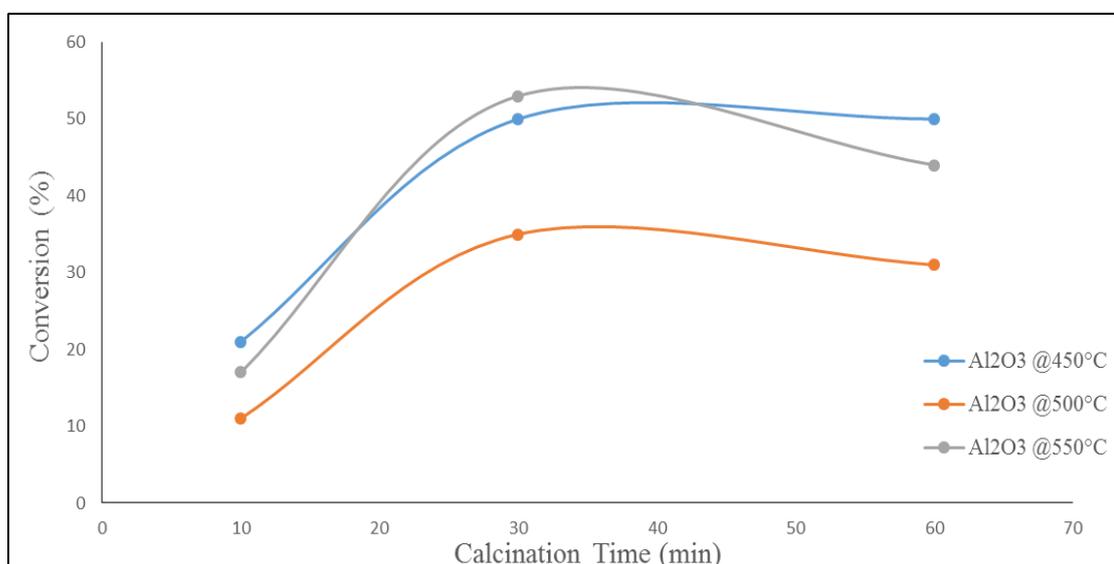


Figure 4.3. Calcination time versus conversion plot for pure alumina samples calcined at 450°C, 500°C and 550°C

According to Figure 4.3., increasing calcination time has reverse impact on oil conversion for all the pure alumina coated samples which were calcined at 450°C, 500°C and 550°C. Canola oil conversion may be reduced because of decreasing activity of the catalyst by increasing calcination time.

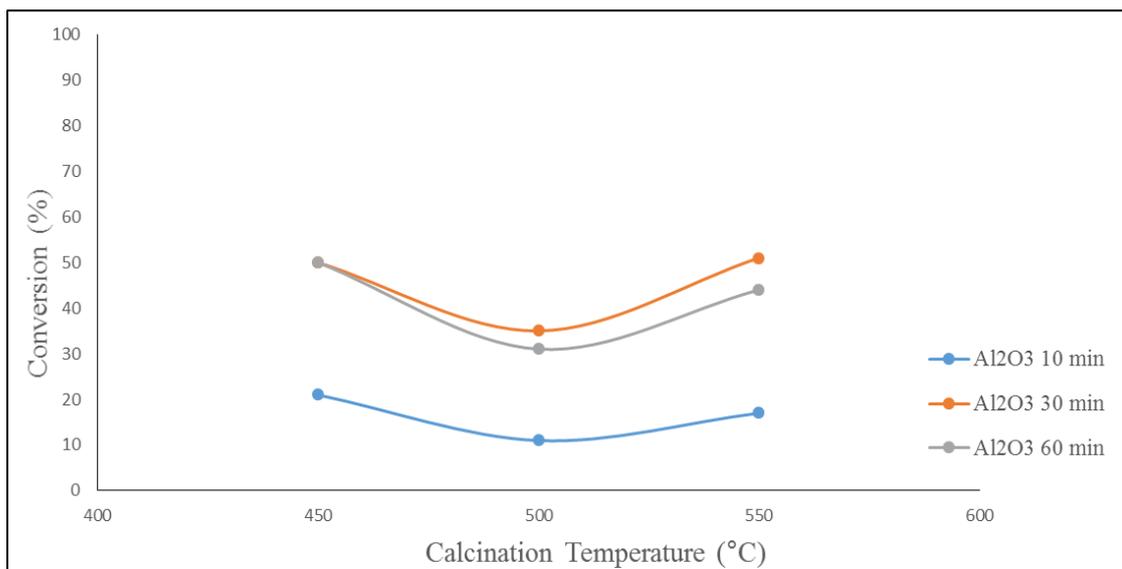


Figure 4.4. Calcination temperature versus conversion plot for pure alumina samples calcined for 10min, 30min, and 60min

Also in Figure 4.4, the impact of calcination temperature on canola oil conversion was indicated for each catalyst synthesized by different calcination times. Increasing calcination temperature has been affected each alumina coated sample differently that has different calcination time. The activity of samples were influenced both calcination time and temperature.

Actually it is expected that alumina would not be active for canola oil combustion reaction. However, the results have been shown that the mass conversion of oil was occurred. This mass loss can be caused by due to evaporation of the coating, not because of the oil conversion into CO₂.

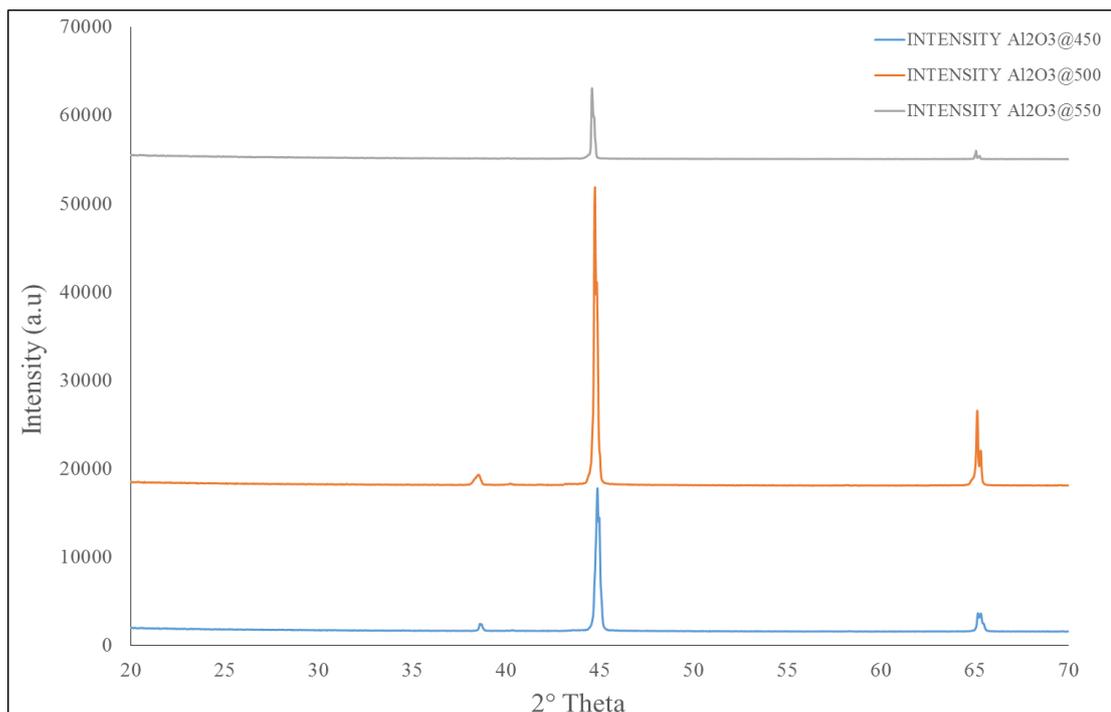


Figure 4.5. XRD Patterns for pure alumina coated samples calcined at 450°C, 500°C, and 550°C for 30 min

The XRD patterns for pure alumina coated samples calcined at 450°C, 500°C, and 550°C for 30 minutes were given in Figure 4.5. Observed peaks were varied with the calcination temperature. The highest peak was obtained for 500°C of calcination temperature. The crystallite sizes were affected by the calcination temperature for pure alumina samples.

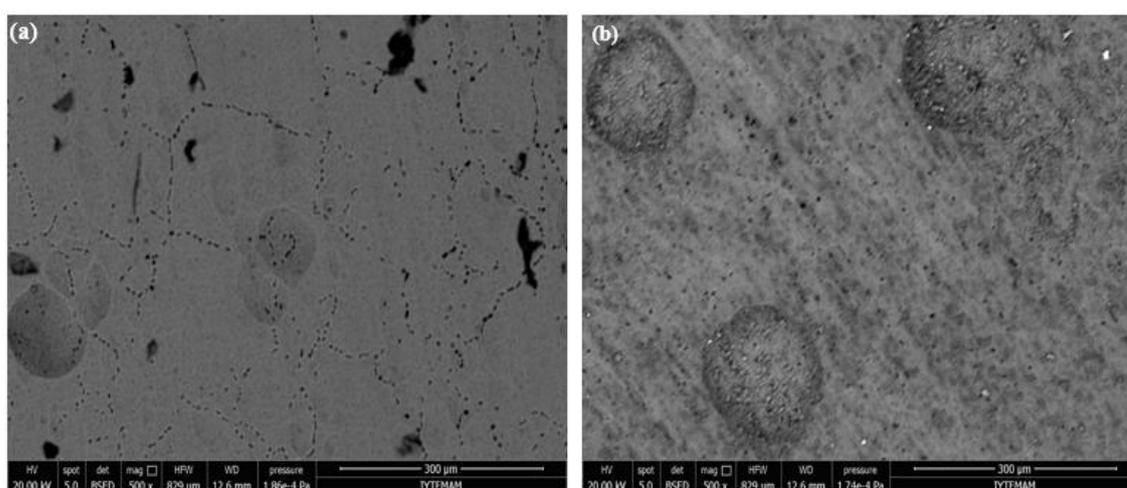


Figure 4.6. SEM images of (a) fresh Pure Alumina coated plate and (b) regenerated Pure Alumina coated plate

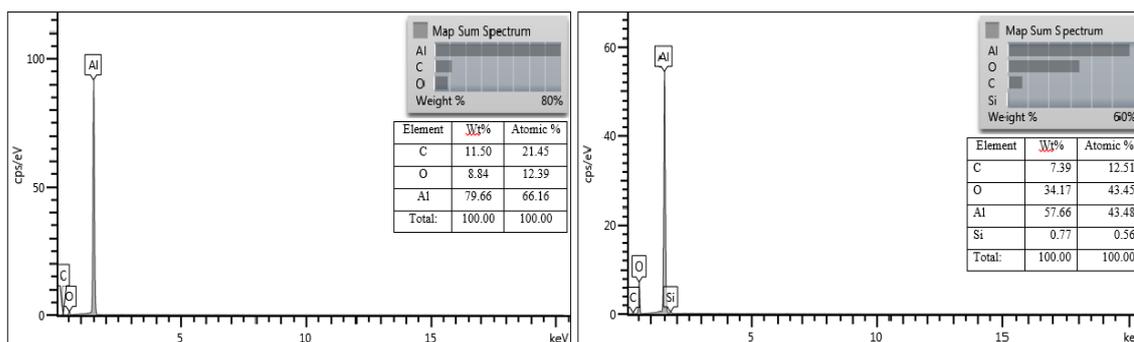


Figure 4.7. EDX Analysis of (a) fresh pure alumina coated plate and (b) regenerated Pure Alumina coated plate

In Figure 4.6., SEM analysis for pure alumina coated fresh sample and regenerated sample were given. The term regenerated indicates that the oil combustion reaction was carried out over the coated samples and then again the sample kept at the calcination temperature remove the remaining oil over the surface.

In Figure 4.7., EDX Analysis of the fresh and regenerated pure alumina samples were shown. According to EDX analysis, with regeneration, the oxygen amount over the surface is increasing since the reducible metals present over surface provides new oxide formations and attaching of the oxygen elements to the surface. Also regenerated surface exposed to reaction temperature and calcination temperature, so that the carbon content was varied. The carbon content over the surface was decreased with regeneration due to breaking of C-C and C-H bonds.

4.2. Aluminum Oxide Supported Nickel Catalyst

The first studied catalyst precursor was nickel acetate supported by aluminum oxide. Nickel oxides have a very strong ability to break C-C bonds resulting electron rich carbon bonds by the cross coupling reactions. Therefore, involving nickel oxides in the oil combustion reactions provides suitable catalytic activity. Also, Prof. Dr. Erol Şeker Research Group have been revealed that performance of nickel catalysts was highly active for the combustion of hydrocarbon compounds. The catalytic coating materials were prepared by nickel acetate monohydrate with 20% Ni/Al₂O₃. The canola oil conversion data for 20% Ni/Al₂O₃ was given in Table 4.4 whose reaction was accomplished at 200°C for 1h.

Table 4.4. Canola oil combustion data for 20% Ni/Al₂O₃

Ni/Al ₂ O ₃ @450°C		Ni/Al ₂ O ₃ @500°C		Ni/Al ₂ O ₃ @550°C	
Time (min)	Conversion (%)	Time (min)	Conversion (%)	Time (min)	Conversion (%)
10	52	10	56	10	25
30	70	30	73	30	53
60	70	60	71	60	53

The results have been shown that nickel catalyst provides considerable conversion values such as 73% for canola oil combustion. Ni/Al₂O₃ catalyst has given considerably high conversion for the oil combustion reaction. Nickel catalyst involved in the oxidation reactions are preferable since nickel that synthesized by nickel acetate has low crystalline size which provides high nickel dispersion.

In Figure 4.8, the catalytic activity of aluminum oxide supported nickel catalyst in terms of conversion over the canola oil combustion reaction has been shown. The effect of calcination time on oil conversion with different calcination temperatures were indicated in Figure 4.8.

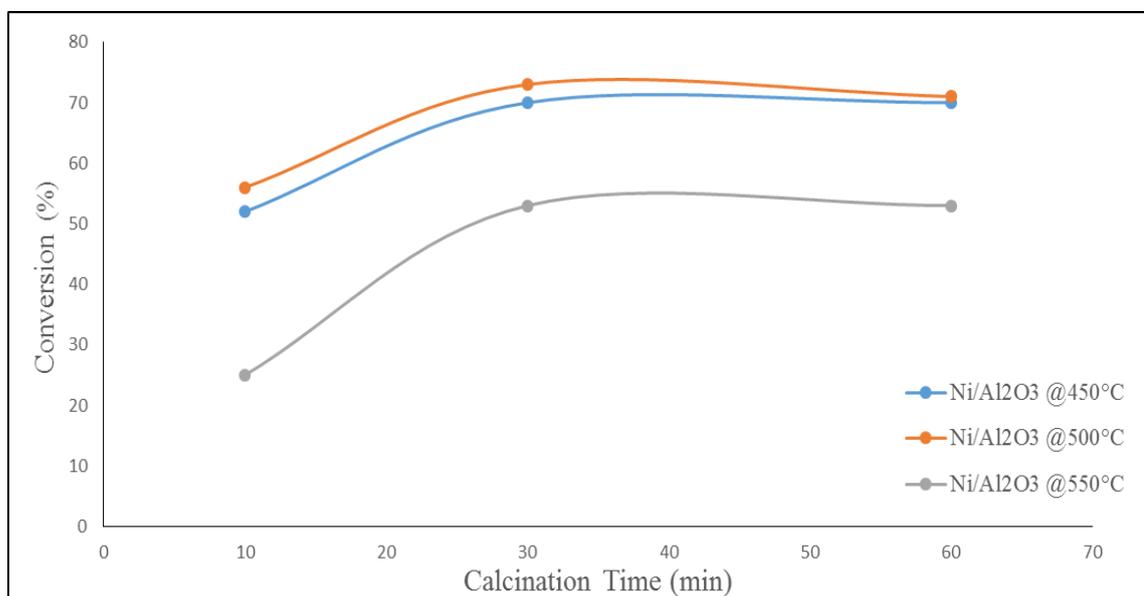


Figure 4.8. Calcination time versus conversion plot for 20% Ni/Al₂O₃ samples calcined at 450°C, 500°C and 550°C

According to Figure 4.8, the calcination time has a positive impact on nickel catalyst performance from 10 to 30 minutes where the 60 minutes of calcination time was

not effective on catalytic performance. Calcination time exceeding 30 minutes has not affected the catalytic activities of Ni/Al₂O₃.

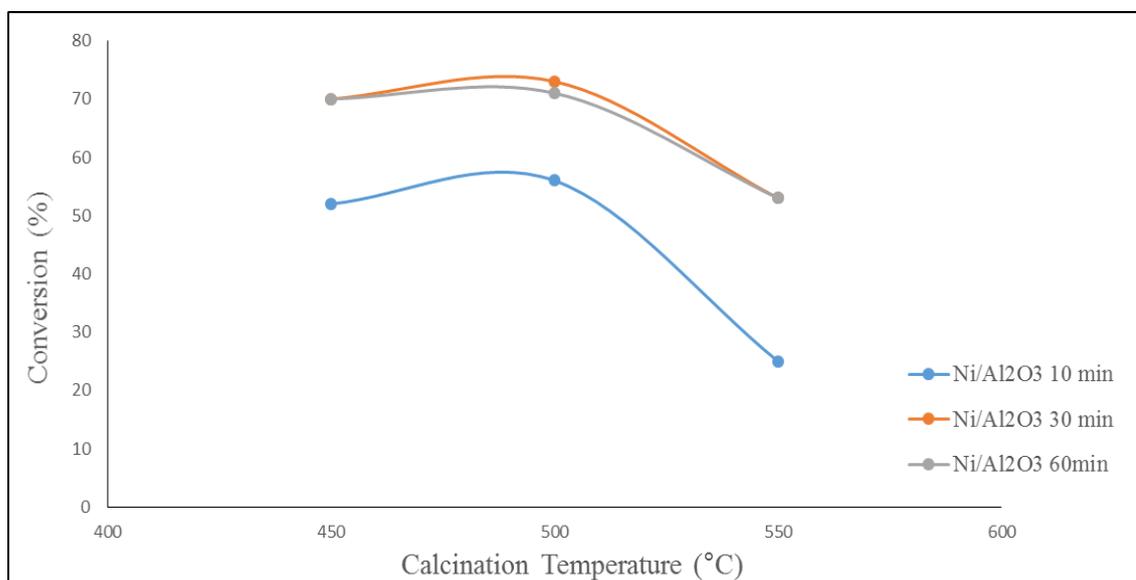


Figure 4.9. Calcination temperature versus conversion plot for 20% Ni/Al₂O₃ samples calcined for 10 min, 30 min, and 60 min

In Figure 4.9, calcination temperature effect on conversion of canola oil was shown. According to Figure 4.9, the increasing calcination temperature has reverse impact on catalytic conversion of canola oil. 550°C of calcination temperature reduces the catalytic conversion. This may be caused because of increasing temperature reduces the activity of 20% Ni/Al₂O₃, thus the ability of breaking C-C bonds would be inhibited.

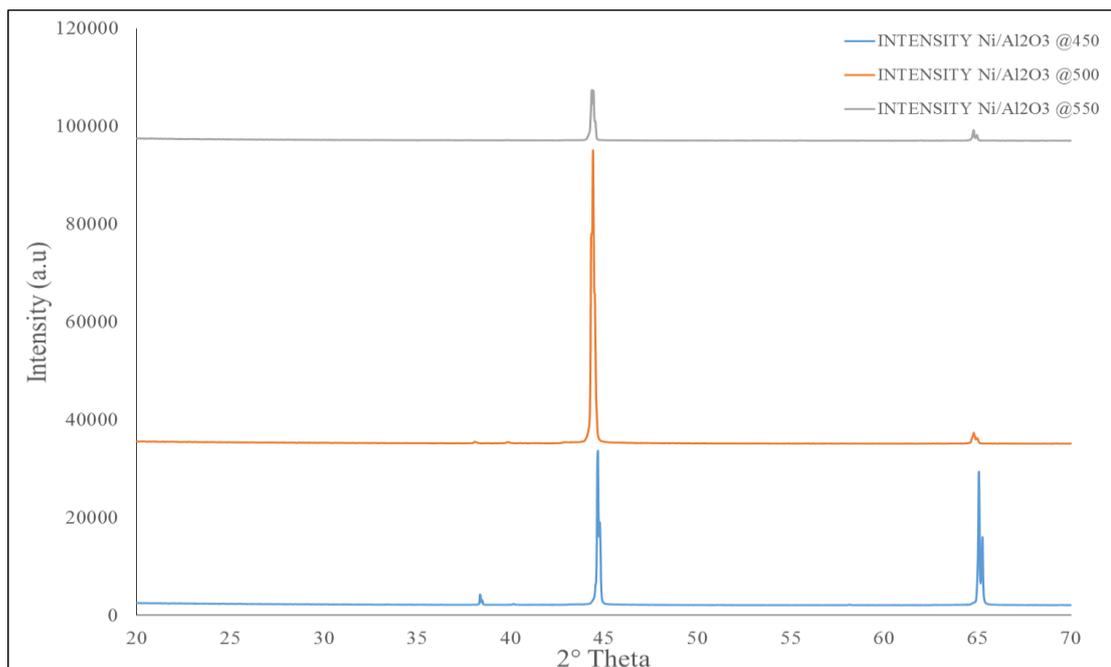


Figure 4.10. XRD Patterns for 20%Ni/Al₂O₃ coated samples calcined at 450°C, 500°C, and 550°C for 30 min

In Figure 4.10. XRD patterns for 20%Ni/Al₂O₃ coated samples calcined at 450°C, 500°C, and 550°C for 30 minutes were given. The same peaks were detected for each of calcination temperature. However, again for 20%Ni/Al₂O₃ catalyst the calcination temperature was affected to the crystallinity of the samples. The highest peak was observed for the sample calcined at 500°C.

In Figure 4.11., SEM images of fresh 20% Ni/Al₂O₃ coated plate and regenerated 20% Ni/Al₂O₃ coated plate samples were given.

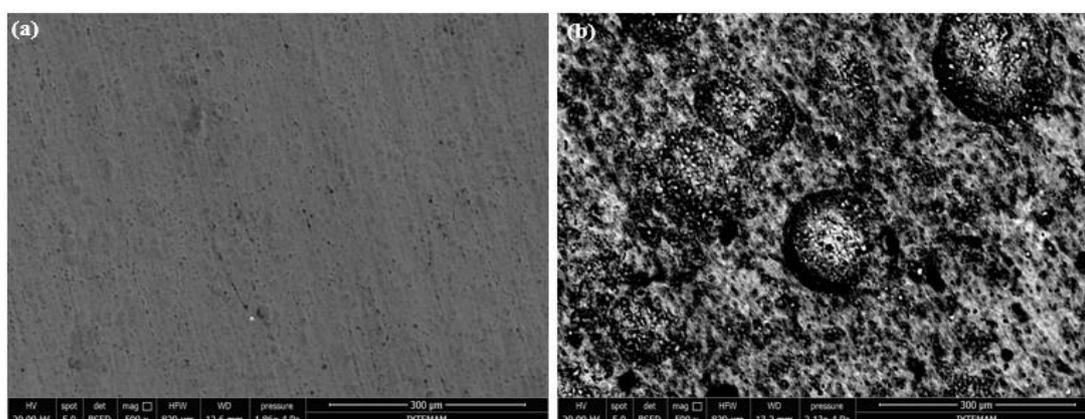


Figure 4.11. SEM images of (a) fresh 20%Ni/Al₂O₃ coated plate and (b) regenerated 20%Ni/Al₂O₃ coated plate

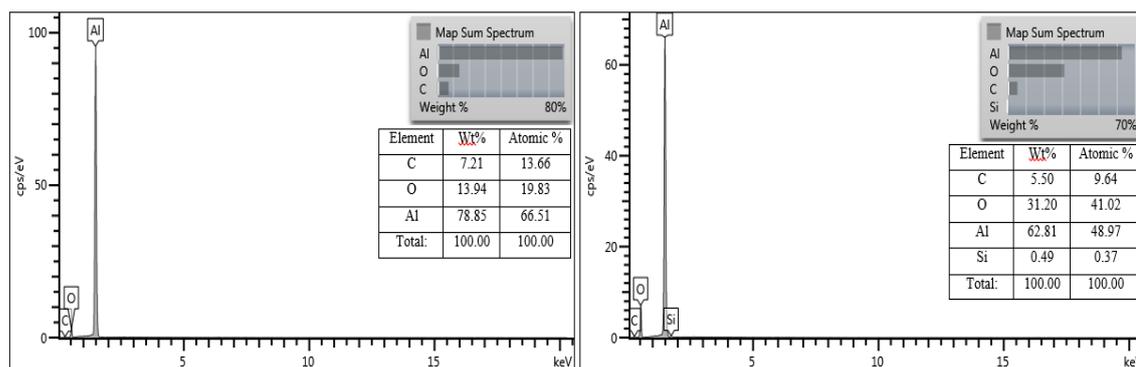


Figure 4.12. EDX Analysis of (a) fresh 20% Ni/Al₂O₃ coated plate and (b) regenerated 20% Ni/Al₂O₃ coated plate

In Figure 4.12. EDX analysis of fresh 20% Ni/Al₂O₃ coated plate and regenerated 20% Ni/Al₂O₃ coated plate were given. After regeneration for 20% Ni/Al₂O₃ sample again the oxygen content was increased, therefore new metal oxide formations would be formed over the surface. Also, the carbon content was decreased by the regeneration. In this case, presence of the nickel in the catalyst also enhanced the ability of breaking C-C and C-H bonds.

4.3. Aluminum Oxide – Manganese Oxide Supported Nickel Catalyst

Another catalyst type for canola oil combustion used for coating was 20%Ni/56%Mn₂O₃/Al₂O₃ which was synthesized by sol-gel method. Manganese oxides are widely used catalysts instead of noble metal catalysts which is given suitable activities for the hydrocarbon oxidation reactions. Also it is known from the literature studies, transition metal oxides are highly reducible for the hydrocarbon total oxidation reactions. Manganese oxides are commonly used catalysts which provides activity and stable for the oxidation reactions with low cost and toxicity. Therefore, in order to accomplish a total oxidation reaction for canola oil mixed oxides which were nickel – manganese mixed oxides were used. To improve the catalytic activity of coated plates, although alumina supported nickel catalysts were provide suitable amount of conversion, manganese oxides were entered to the system. So that, it was aimed to obtain desired product distribution from the canola oil combustion reaction. In Table 4.5, the results of canola oil combustion which were reacted at 200°C for 1h over manganese oxide – aluminum oxide supported nickel coated plates were given.

Table 4.5. Canola oil combustion data for 20%Ni/56%Mn_xO_y/Al₂O₃

20%Ni/56%Mn _x O _y Al ₂ O ₃ @450°C		20%Ni/56%Mn _x O _y Al ₂ O ₃ @500°C		20%Ni/56%Mn _x O _y Al ₂ O ₃ @550°C	
Time (min)	Conversion (%)	Time (min)	Conversion (%)	Time (min)	Conversion (%)
10	67	10	85	10	53
30	76	30	75	30	59
60	84	60	81	60	57

The results have been shown that the highest conversion values were obtained by 20%Ni/56%Mn_xO_y/Al₂O₃. The maximum conversion of oil was 85%. In Figure 4.13, the impact of calcination time on the oil conversion of samples prepared with 450°C, 500°C and 550°C was observed.

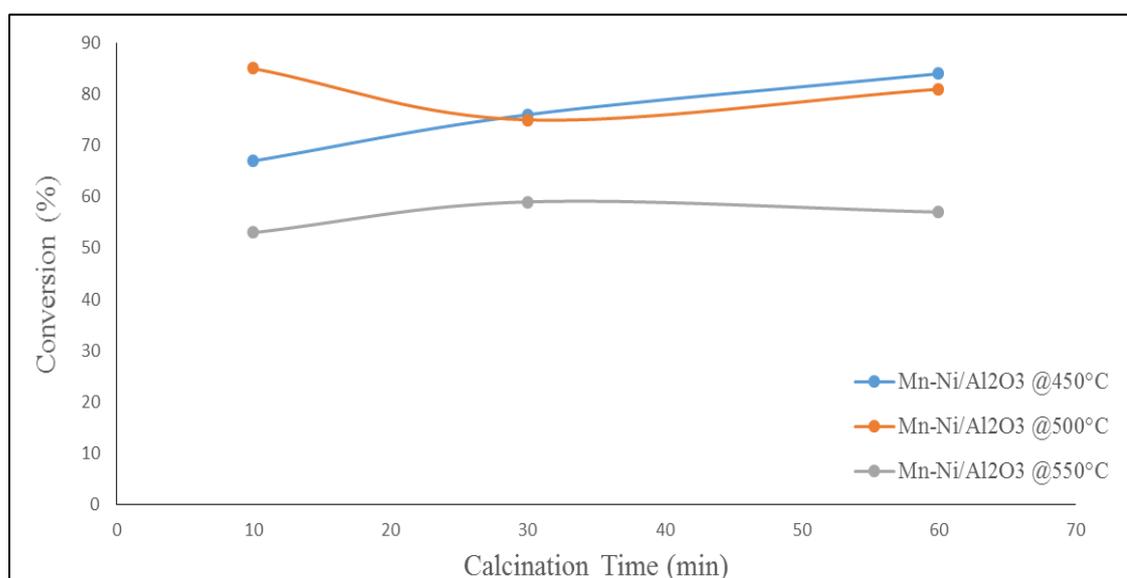


Figure 4.13. Calcination time versus conversion plot for 20%Ni/56%Mn_xO_y/Al₂O₃ samples calcined at 450°C, 500°C and 550°C

Increasing calcination temperature provides higher catalytic activity on the 20%Ni/56%Mn_xO_y/Al₂O₃ samples in terms of oil combustion. Although the highest conversion of 20%Ni/56%Mn_xO_y/Al₂O₃ provided by the samples prepared by 10 minutes of calcination time, the general behavior was more likely to increasing by time.

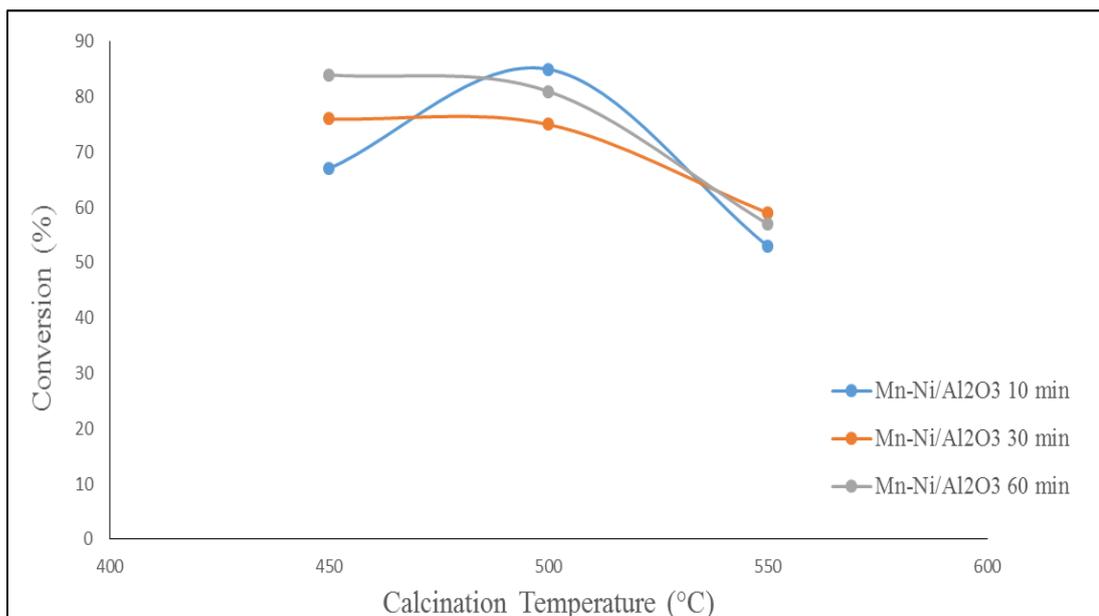


Figure 4.14. Calcination temperature versus conversion plot for 20%Ni/56%Mn_xO_y/Al₂O₃ samples calcined for 10, 30, 60 min

On the other hand, calcination temperature effect on the oil conversion was revealed in Figure 4.14. Increasing calcination temperature was caused to loss of activity of the 20%Ni/56%Mn_xO_y/Al₂O₃ coated samples. 550°C of calcination temperature was probably led to deactivation of the coating or this may be led to evaporation of the coating from the plates. The increasing calcination temperature causes lowering the specific surface areas. This situation leads to decelerating the reaction rate of combustion. Therefore, the oil conversion was decreased with increasing calcination temperature. In this case, 450°C of calcination temperature seems to be not provided enough stabilization for the coatings. 500°C of calcination temperature was the optimum temperature for 20%Ni/56%Mn_xO_y/Al₂O₃ catalyst synthesis.

In these analysis the conversion of the canola oil was calculated in terms of weight loss. However, the coated samples were exposed to high temperatures and may be caused to evaporations on the surface. In spite of pure alumina coated samples were investigated as blank samples, still conversion of oil was observed. This value may be caused by either combustion or combustion and evaporation together. In order to determine what was really occurred on the coated surface, GC-MS and GC-TCD analysis were applied for 20%Ni/56%Mn_xO_y/Al₂O₃ catalyst.

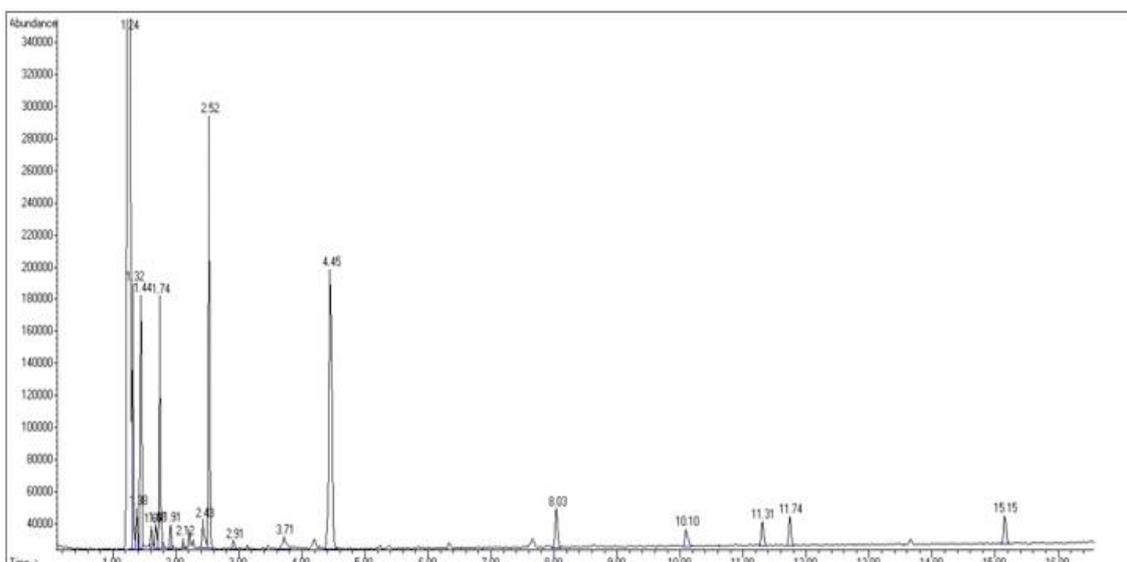


Figure 4.15. GC-MS chromatogram of combustion of oil at 170°C for 1 h by using 20%Ni/56%Mn_xO_y/Al₂O₃

In Figure 4.15., GC-MS chromatogram of combustion of oil over the 20%Ni/56%Mn_xO_y/Al₂O₃ catalyst at the 170°C of reaction temperature for 1 hour of reaction time was shown. According to Figure 4.15., O₂, N₂, CO, CO₂, H₂O and other organic compounds of pentane, propanol, butenal, pentanal were produced at which 1.260,1.442, 1.608 1.740, 2.522 min of the GC-MS analysis, respectively.

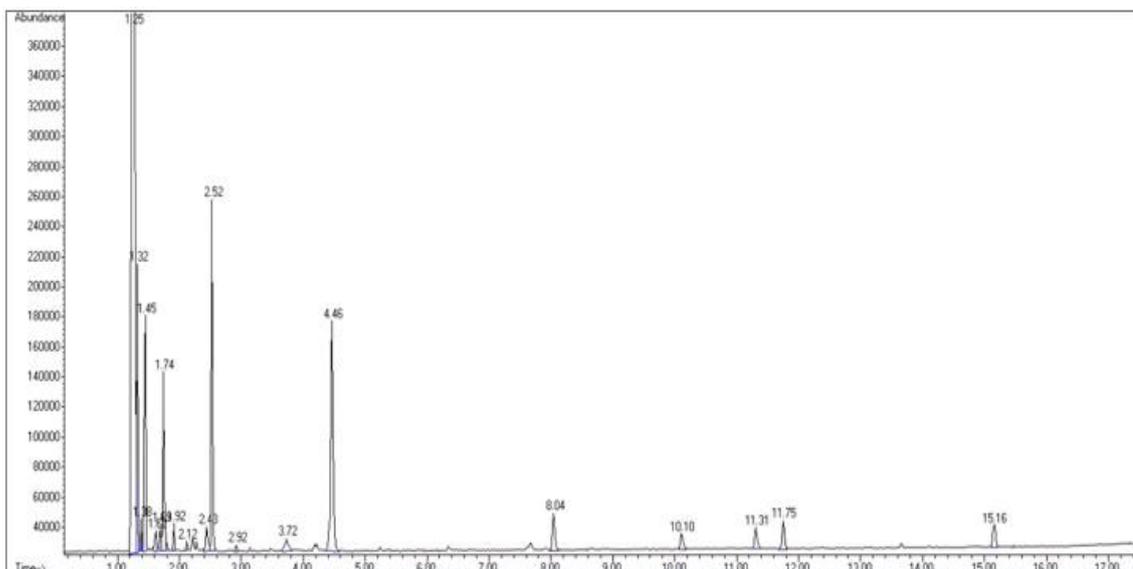


Figure 4.16. GC-MS chromatogram of combustion of oil at 200°C for 1 h by using 20%Ni/56%Mn_xO_y/Al₂O₃

In Figure 4.16., GC-MS chromatogram of combustion of oil over the 20%Ni/56%Mn_xO_y/Al₂O₃ catalyst at the 200°C of reaction temperature for 1 hour of reaction time was shown. According to Figure 4.16., O₂, N₂, CO, CO₂, H₂O and other organic compounds of pentane, propanol, butenal, and pentanal were produced the nearly same peaks with the combustion set-up with 170°C for 1 hour of reaction time. For both chromatograms no compounds detected after 10 minutes.

According to GC-MS analysis for both reaction temperatures were revealed that combustion over the catalysts generates some of the compounds which can be released by the outlet of the oil combustion with the absence of the catalysts as it was proofed by the Prof. Dr. Erol Şeker research group. Therefore, the gas outlet composition for reaction over the 20%Ni/56%Mn_xO_y/Al₂O₃ catalyst was provided the proposed oil reaction mechanism. In Figure 4.17., GC-TCD chromatogram of combustion of oil by using 20%Ni/56%Mn_xO_y/Al₂O₃ at 200°C for 1 hour of reaction was given.

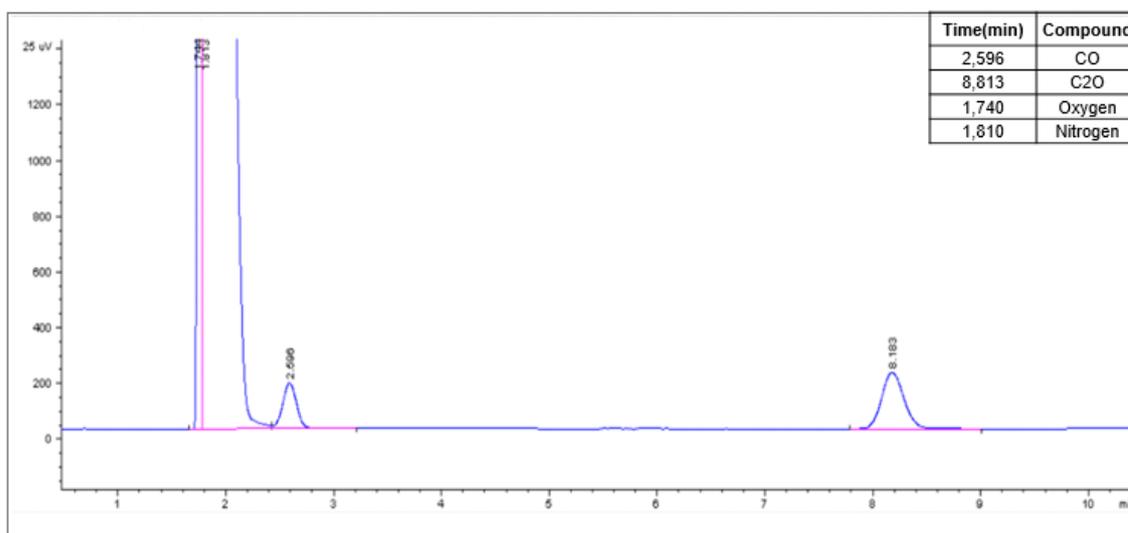


Figure 4.17. GC-TCD chromatogram of combustion of oil at 200°C for 1 h by using 20%Ni/56%Mn_xO_y/Al₂O₃

According Figure 4.17., CO, CO₂, O₂, N₂ compounds were detected at which 2.596, 8.813, 1.740, and 1.810 minutes of the analysis, respectively. GC-MS and GC-TCD analysis were revealed that the combustion reaction was accomplished over the 20%Ni/56%Mn_xO_y/Al₂O₃ catalyst.

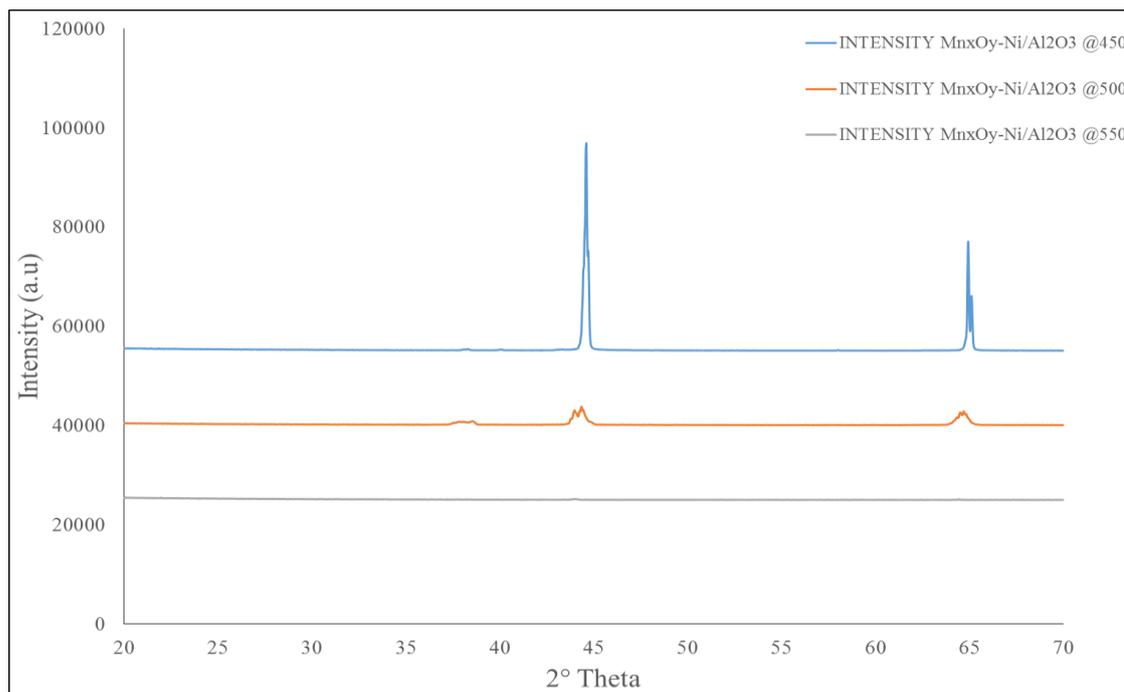


Figure 4.18. XRD Patterns for 20%Ni/56% Mn_xO_y/Al_2O_3 coated samples calcined at 450°C, 500°C, and 550°C for 30 min

In Figure 4.18., XRD Patterns for 20%Ni/56% Mn_xO_y/Al_2O_3 coated samples calcined at 450°C, 500°C, and 550°C for 30 minutes were given. For 20%Ni/56% Mn_xO_y/Al_2O_3 coated samples increasing calcination temperature reduces the intensity. The observed peaks of the samples were reduced by the increasing calcination temperature. Therefore, the 550°C of calcination temperature is not suitable for 20%Ni/56% Mn_xO_y/Al_2O_3 coated samples in terms of crystallinity.

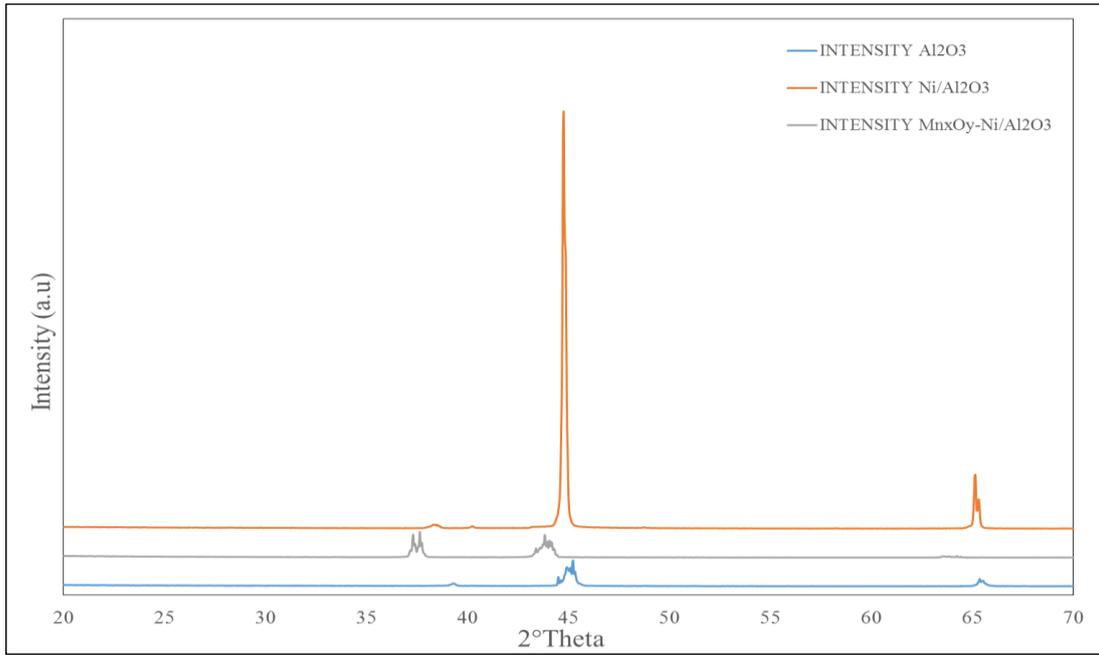


Figure 4. 19. XRD Patterns for fresh pure alumina, 20%Ni/Al₂O₃, and 20%Ni/56% Mn_xO_y/Al₂O₃ coated samples

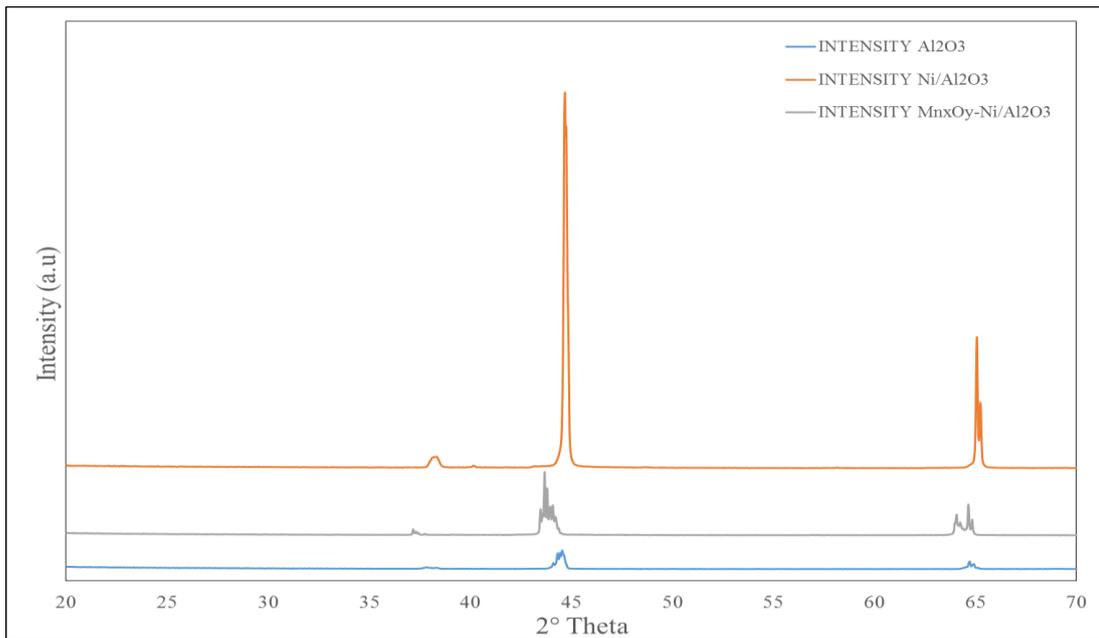


Figure 4. 20. XRD Patterns for regenerated pure alumina, 20%Ni/Al₂O₃, and 20%Ni/56% Mn_xO_y/Al₂O₃ coated samples

In Figure 4.19., XRD patterns for fresh pure alumina, 20%Ni/Al₂O₃, and 20%Ni/56%Mn_xO_y/Al₂O₃ coated samples were given. In Figure 4.20., XRD patterns for regenerated pure alumina, 20%Ni/Al₂O₃, and 20%Ni/56%Mn_xO_y/Al₂O₃ coated samples were given. According to Figure 4.19. and Figure 4.20., the largest peak belongs to Ni.

For both fresh and regenerated samples, the crystallite size of Ni were calculated as 48.4 nm. Therefore, the crystallinity was not affected by the regeneration which means that catalyst was not sintered. According to Figure 4.19. and Figure 4.20., the large Ni peak was not observed for 20%Ni/56%Mn_xO_y/Al₂O₃. Involving the combination of Mn and Ni changes the crystal size of the Ni, since, XRD is not detected less than 5 nm in size.

In Figure 4.21. SEM images of fresh 20%Ni/56%Mn_xO_y/Al₂O₃ coated plate and regenerated 20%Ni/56%Mn_xO_y/Al₂O₃ coated plate samples were given. 20%Ni/56%Mn_xO_y/Al₂O₃ due to surface structure, the manganese were penetrated to the surface easily which was caused to acceleration of the reaction.

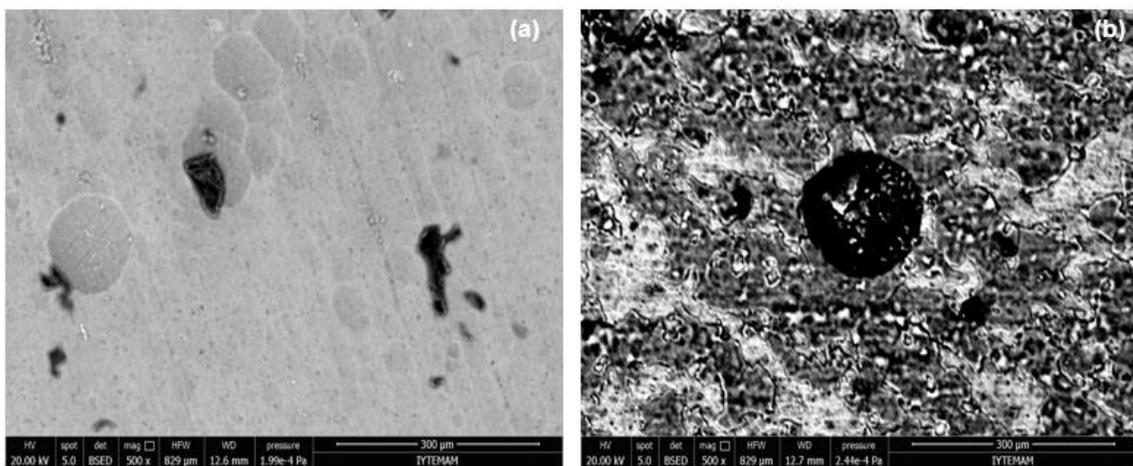


Figure 4.21. SEM images of (a) fresh 20%Ni/56%Mn_xO_y/Al₂O₃coated plate and (b) regenerated 20%Ni/56%Mn_xO_y/Al₂O₃ coated plate

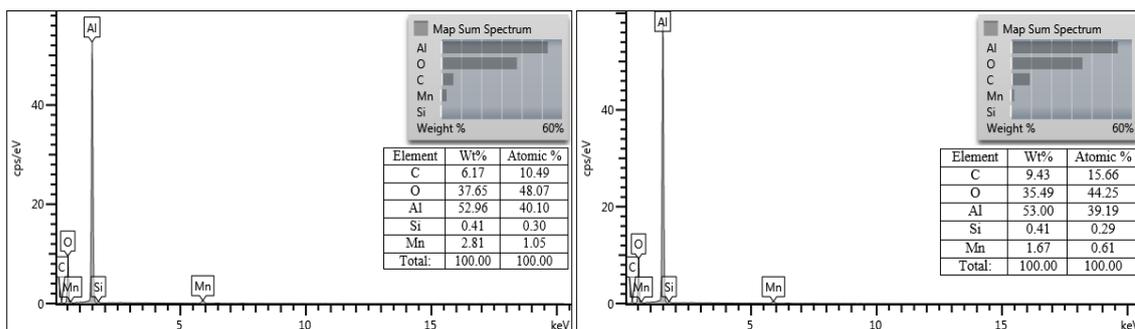


Figure 4.22. EDX Analysis of (a) fresh 20%Ni/56%Mn_xO_y/Al₂O₃coated plate and (b) regenerated 20%Ni/56%Mn_xO_y/Al₂O₃ coated plate

According to EDX analysis of fresh 20%Ni/56%Mn_xO_y/Al₂O₃ coated plate and regenerated 20%Ni/56%Mn_xO_y/Al₂O₃ coated plate samples given in Figure 4.22., the manganese content was decreased by the regeneration. The impact of the regeneration

was varied for the 20%Ni/56%Mn_xO_y/Al₂O₃ samples for the carbon, oxygen and aluminum elements. The elemental distribution was affected by the presence of the manganese elements.

4.4. Reusability of the Catalysts

The reusability tests were conducted for all types of the catalysts to evaluate the performance of the catalyst in the second usage. In Figure 4.23., the effect of catalyst usages on the conversion were given.

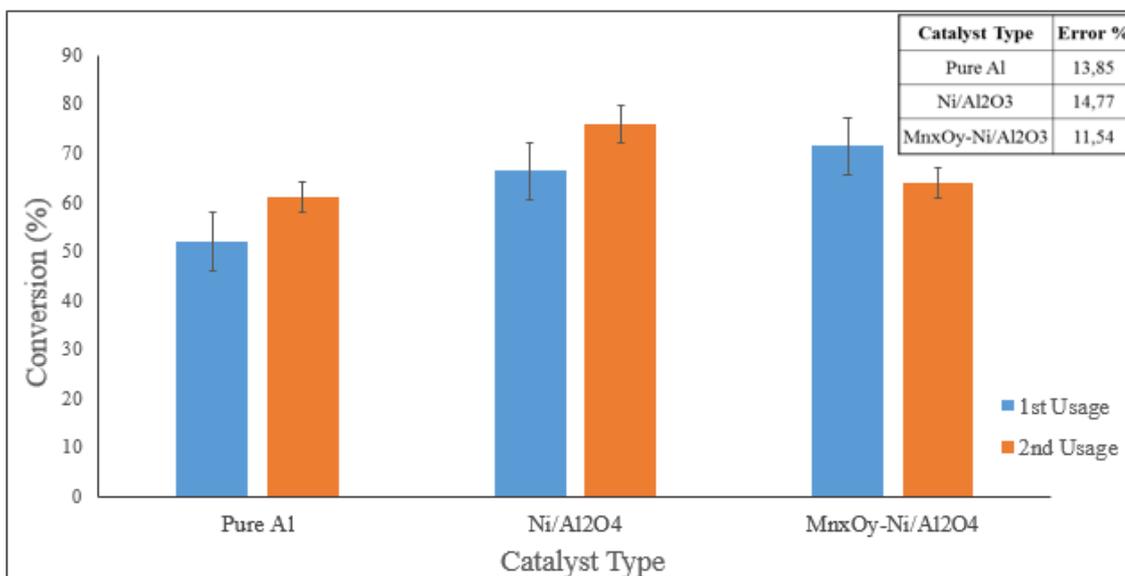


Figure 4.23. Reusability Plot of Catalysts by 30 min of Calcination @170°C for 1h

Pure alumina and 20% Ni/Al₂O₃ were provided higher conversions in the second usage. For the 20%Ni/56%Mn_xO_y/Al₂O₃ catalyst conversion was decreased in the second usage. According to calculated error percentages the conversion values were not exceed the error ranges. Therefore, for each type of catalyst, no considerable performance lost was observed.

4.5. Factorial Analysis of the Study

In this study a statistical model was conducted in order to verify the experimental results. The model was constructed via Minitab v.17® in order to determine the effect of factors and their interactions on the response. In this case the factors were catalysts type, calcination time and calcination temperature whereas the response was conversion. In Table 4.6., the factors and their levels were shown.

Table 4.6. Factors and Levels

Factors			Response
Levels	Catalyst Type	Calcination Temperature (°C)	Calcination Time (min)
	Pure Al ₂ O ₃	450	10
	Ni/Al ₂ O ₃	500	30
	Mn _x O _y - Ni/Al ₂ O ₃	550	60

Three factors present which were catalyst type, calcination time and temperature with three levels, general full factorial model was constructed to describe the system. In this case, experimental results of 3³ runs were collected to build the model. In this study single replication was conducted due to limited raw materials. In Table 4.7, the results of first constructed model was indicated where the P-values of the factors and interactions cannot be calculated due to usage of single replication model. In that case, significance of the factors and interactions are evaluated according to their adjusted sum of squares. By that method, three way interactions and two way interactions of catalyst time and temperature are found as insignificant due to their low adjusted sum of squares.

Table 4.7. Analysis of Variance for all interactions and factors

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Model	26	1.09916	0.042275	*	*
Linear	6	0.84222	0.140370	*	*
Cat. Type	2	0.57103	0.285515	*	*
Cal. Time	2	0.18527	0.092637	*	*
Cal. Temp.	2	0.08592	0.042959	*	*
2-Way Interactions	12	0.24564	0.020470	*	*
Cat. Type*Cal. Time	4	0.07479	0.018698	*	*
Cat. Type*Cal. Temp.	4	0.14528	0.036320	*	*
Cal. Time*Cal. Temp.	4	0.02557	0.006393	*	*
3-Way Interactions	8	0.01130	0.001412	*	*
Cat. Type*Cal. Time*Cal. Temp.	8	0.01130	0.001412	*	*
Error	0	*	*		
Total	26	1.09916			

Insignificant terms were eliminated which were taken as residuals. Then model was run again and the results were given in Table 4.8. Although, two way interactions of catalyst type and calcination time seems like insignificant for the confidence level of 95%, it was significant for confidence level of 90%, thus that terms was not eliminated and involved in the model.

Table 4.8. Analysis of Variance for selected interactions of factors

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Model	14	1.06230	0.075878	24.70	0.000
Linear	6	0.84222	0.140370	45.69	0.000
Cat. Type	2	0.57103	0.285515	92.93	0.000
Cal. Time	2	0.18527	0.092637	30.15	0.000
Cal. Temp.	2	0.08592	0.042959	13.98	0.001
2-Way Interactions	8	0.22007	0.027509	8.95	0.000
Cat. Type*Cal. Time	4	0.07479	0.018698	6.09	0.007
Cat. Type*Cal. Temp.	4	0.14528	0.036320	11.82	0.000
Error	12	0.03687	0.003072		
Total	26	1.09916			

In Figure 4.24, the interaction plot of oil combustion conversion was given. In the interaction plots, the crossing lines indicates that the factors interacts each other.

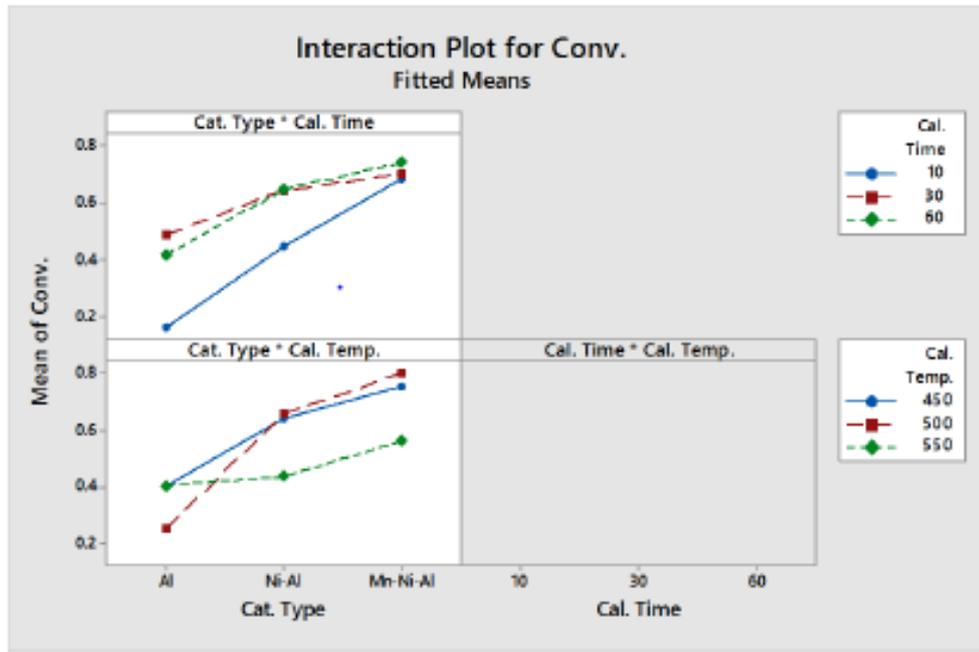


Figure 4.24. Interaction plots for conversion of oil combustion reaction

According to Figure 4.24., the catalysts type strongly affected by the calcination times of 30 minutes and 60 minutes. On the other hand, the all the levels of the calcination temperature have a strong impact on the catalyst type. Furthermore, in Figure 4.25., the main effects plot for the response which is conversion was given. The main effect plot indicates the effects of the factors individually on the response.

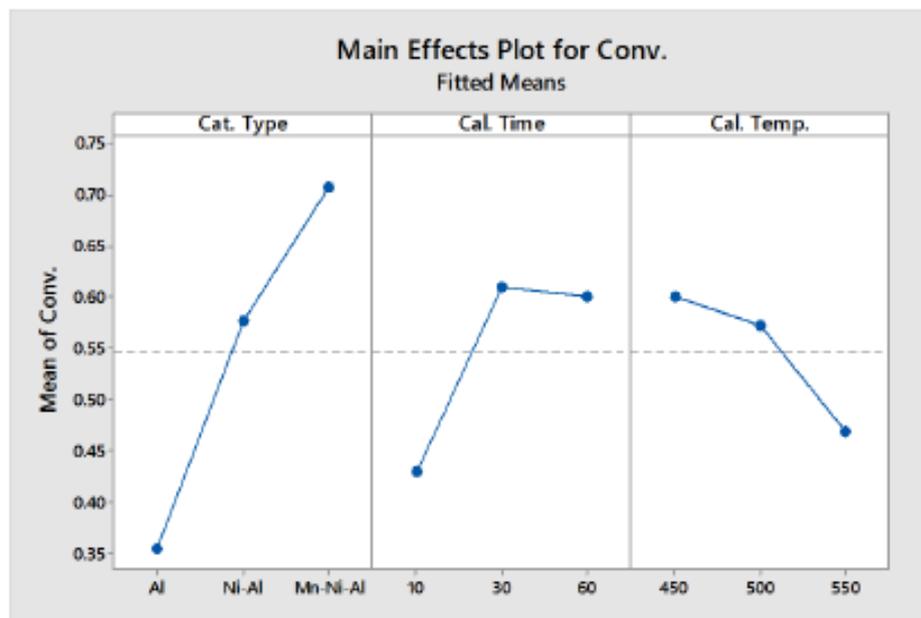


Figure 4.25. Main effects plot for conversion of oil combustion reaction

According to Figure 4.25, all the three factors have significant impact on the mean of conversion. The catalyst type from pure alumina to aluminum oxide – manganese oxide supported nickel catalyst the have a positive impact on the conversion. The calcination time from 10 minutes to 30 minutes increases the conversion whereas after 30 minutes slightly decreases the conversion. Also the calcination temperature has a reverse effect on the conversion. The results from main effect plot were verified the experimental results. In order to predict the accuracy of the model, R-square values must be checked. In Table 4.9., the model summary was given.

Table 4.9. Model Summary of selected interactions of factors

S	R-sq	R-sq(adj)	R-sq(pred)
0.0554276	96.65%	92.73%	83.02%

According to Table 4.9., R-square values have been shown that the model is significant. Predicted R-square value is the most critical value to determine the significance of the model which is 83.02%. Therefore, the model is applicable.

Another indication of accuracy of the model prediction was the distribution of residuals. Firstly, normal probability plot was checked to determine the residual distribution with 95% confidence level. In Figure 4.26., the residual plot was given. According to Figure 4.26., with 95% of accuracy there were no outliers, so that the residuals were distributed normally. Similarly, in the residual vs fits and results vs. order graphs, there were no pattern of distribution of residuals. The random distribution of the data points is an important factor, since it indicates that data points are not repeated.

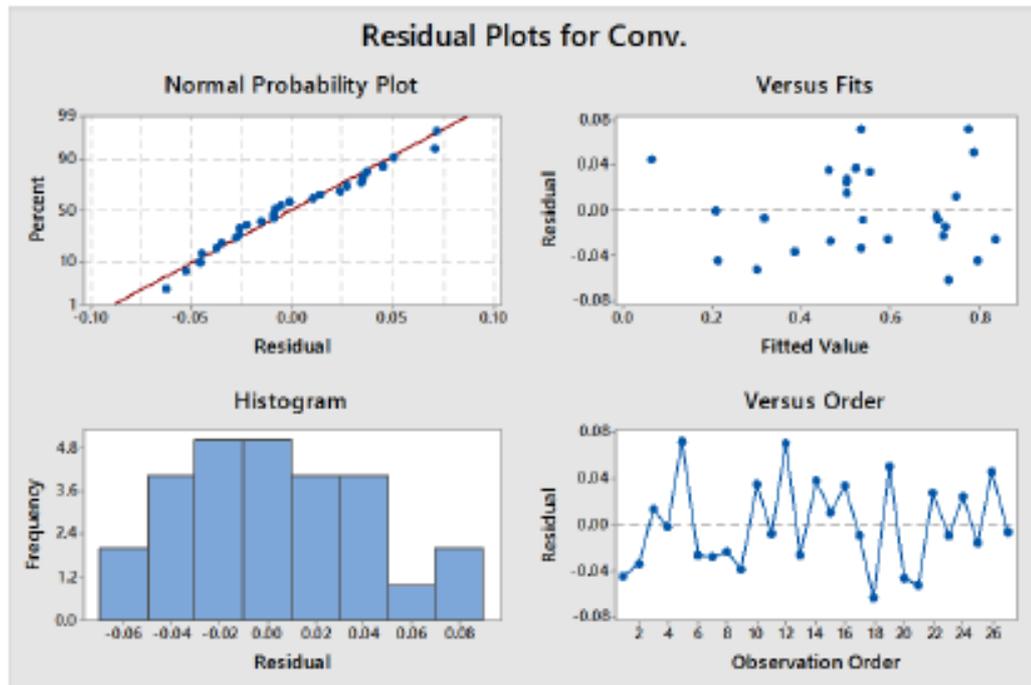


Figure 4.26. Residual plots for conversion of oil combustion reaction

Model predicts good enough to estimate future data points, real experiment conditions cannot be same all the time, which affects the results of the experiments. However, the behaviors of the factors on the conversion provides required information about further levels of the experiments.

CHAPTER 5

CONCLUSION

Ovens are required tools for cooking processes which are full fill the most parts of the human lives such as bakery or meal preparation. As it is known, cooking is a heat involved process that causes oils present in bakeries or meals evaporates and contaminates the oven walls. Cleaning of these contaminated oil over the oven surfaces consumes time, energy and cleaning products. Self-cleaning surfaces must be considered to reduce the amount of these contaminated oil. In this study, self-cleaning surfaces are basically provided by coated surfaces with catalyst that is not harm the human health. The catalyst on the surface provides the combustion of oil attached to the surface with the heat and turn it into stack gas to eliminate them with oven fan.

In this study, in order to accomplish that purpose, several catalyst types, surface and preparation methods have been employed and tested with oil combustion reaction. The oil combustion reaction was carried at 170°C and 200°C for 1h for each type of catalysts. The studied catalysts which were catalytic coating materials were pure alumina, 20%Ni/Al₂O₃ and for 20%Ni/56%Mn₂O₃/Al₂O₃. The coating materials were prepared with sol-gel method and coated to the aluminum plates by dip-coating with constant immersing and withdrawal speed.

The impacts of calcination time and calcination temperature on the catalytic activity of the coatings were investigated. Because those parameters are highly affected to the catalytic activity of the catalytic coatings. The studied calcination temperatures were 450°C, 500°C and 550°C where the calcination times were 10 min, 30 min and 60 min. According to the oil combustion conversion results the most active catalyst was for 20%Ni/56%Mn₂O₃/Al₂O₃ prepared with 500°C of calcination temperature for 30 minutes. General trend of the results have been provided that increasing calcination temperature decreases the catalytic activity while the calcination time has positive impact on for 20%Ni/56%Mn₂O₃/Al₂O₃ samples. In this situation was not the same for 20%Ni/Al₂O₃ catalyst. In that case, again calcination temperature decreases the oil conversion and calcination time increases the conversion. Since the optimum condition for both catalysts

was 500°C of calcination temperature and 30 minutes of calcination time. Because after 30 minutes the catalytic activity of the catalysts were not considerably changed whereas 10 minutes of calcination time was not enough to provide higher conversions of oil.

GC-MS and GC-TCD analysis have been shown that the oil combustion over the prepared catalyst coated surfaces was provided according to outlet gases. Also according to GC-MS analysis the outlet compounds from the oil combustion were also can be observed from the oil combustion with absence of the catalysts.

According to conducted analysis, the crystallite size for 20%Ni/Al₂O₃ is equal for fresh and regenerated samples, so that no sintering exist for the catalyst. Combining Ni and Mn, reduces the crystallite size of Ni since XRD is not detect the crystals lower than 5 nm in size.

A general factorial design was employed for this study to check the significance of the model. Model of the study was constructed by Minitab® v.17 to determine the catalytic behavior with altering factors. In this model, catalyst type, calcination time and calcination temperature were the selected factors for the oil combustion reaction where the catalytic conversion of oil to stack gas was the response of the model. This model has been shown that calcination time has positive effect on conversion whereas increasing calcination temperature reduces the conversion. According to constructed model best catalyst was chosen as for 20%Ni/56%Mn₂O₃/Al₂O₃ calcined at 500°C for 30 minutes.

If the constructed models prediction capability is investigated was observed that, all the residuals are distributed normally and R-square prediction was found as 83%. Also, it is observed that two way interactions of the factors are significantly affects the system, and factors' levels should be changed accordingly.

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